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PART ONE

**INTRODUCTION
TO
ORGANIC CHEMISTRY**

Chapter 1

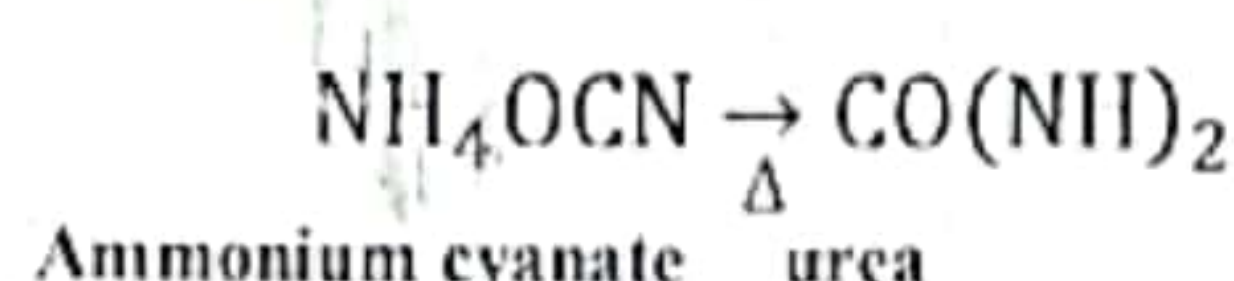
ORGANIC COMPOUNDS

At one time, chemists believed that organic compounds were fundamentally different from those that were inorganic because organic compounds contained a **vital force** that was only found in living systems. Thus according to this concept, organic compounds can only be created by living organisms.

- These chemists divided materials into two categories. Those isolated from plants and animals were classified as **organic** (derived from the word 'organism'), while those that trace back to minerals were **inorganic**.

So with this point of view organic chemistry can simply be defined as the study of compounds of carbon derived from living things.

- However nowadays it is possible to synthesize organic compounds like urea (from inorganic compounds!) which previously was observed only in living tissue.



Organic Chemistry has undergone a large change such that there are over a million synthetic organic compounds like plastics.

- The important thing to note about organic compounds is that, they all contain carbon atom(s) although there are few exceptional compounds of carbon which do not behave like organic and therefore they are termed as inorganic.

What is organic chemistry?

By definition, **organic chemistry** is the branch of chemistry that deals with the study of carbon compounds excluding simple compounds like oxides of carbon (CO, and CO₂), carbonates, hydrogencarbonate, carbon disulphide, cyanides and carbides.

SOURCES OF ORGANIC COMPOUNDS

Main sources of organic compounds are living organisms that are plants and animals. The various organic compounds have been artificially prepared in the laboratory.

- Some important sources of organic compounds have been listed below.

(i) Plants and animals

Many organic compounds are obtained directly from plant and animal sources. This includes carbohydrates (cellulose, sugar, and starches), proteins, fats and oils, hormones and vitamins.

(ii) Natural gas and petroleum

Natural gas and petroleum are among the major sources of organic compounds.

- They are used as fuels and also, through synthetic organic reaction, for the production of hundreds of useful organic substances such as solvents, synthetic rubber, explosive, and plastic.

(iii) Coal

Coal is another major source of organic compounds. It yields coke and coal-tar on pyrolysis (*The thermochemical decomposition of organic material at very high temperature in the absence of oxygen or any halogen*) or destructive distillation (*A process by which organic substances such as wood, coal, and oil shale are decomposed by heat in the absence of air and distilled to produce useful products such as coke, charcoal, oils, and gases*).

- Many organic compounds have been directly isolated from coal-tar. These coal-tar products from the starting materials for the manufacture of thousands of useful aromatic compounds, including perfumes, drugs and dyes.

(iv) Synthesis

Simple organic compounds derived from petroleum or coal has been converted into thousands of useful materials by synthetic method.

- This includes dyes, rubber, fibres, plastic, drugs, and vitamins.

UNIQUENESS OF CARBON

Carbon forms a very large number of compounds (over 4,000,000!). This is far more than the number of compounds of all other elements put together which is less than 100,000. Carbon has this unique property of forming so many compounds because of reasons explained below.

(i) Ability of forming multiple bond

Carbon can form single, double and triple bonds.

- Carbon can form multiple bond with other carbon atoms ($C = C$ and $C \equiv C$).
- It can also form multiple bonds with atoms of other elements such as oxygen, sulphur and nitrogen in $C = O$, $C = S$, and $C \equiv N$ respectively.

Ability of carbon to form multiple bonds is explained by its small atomic radius which enables it to form strong covalent bond even through sideways overlapping of atomic orbitals in pi bond formation, the condition which is necessary for multiple bond formation.

(ii) Ability of undergoing different types of hybridisation

Carbon can undergo sp^3 , sp^2 and sp hybridisation.

- sp^3 hybridisation provides the basis of formation of single covalent bond with another atom.
- sp^2 hybridisation atom provides the basis of formation of double bond with another atom.
- sp hybridisation provides the basis of formation of triple bond with another atom.

(iii) High ability of forming covalent bonds

Carbon having four valence electrons in $2s^2 2p^2$, in forming ionic bond it must either gain four electrons or lose four electrons to reach a noble (or rare) gas configuration.

- Being in group IVA, the electronegativity of carbon is too small for carbon to gain electrons from most elements to form C^{4-} ions, and too large for carbon to lose electrons to form C^{4+} ions.
- Carbon therefore forms covalent bonds with a large number of other elements, including the hydrogen, nitrogen, oxygen, phosphorus, and sulphur found in living systems.

(iv) Ability of undergoing catenation

Catenation is the bonding of atoms of the same element into longer and stable chain. The chain may be open or cyclic, branched or straight.

- Carbon can undergo catenation because it has comparative small atomic size and small repulsion between its valence electrons.

DIFFERENCES BETWEEN ORGANIC AND INORGANIC COMPOUNDS

Organic and inorganic compounds possess different composition, nature, structure, and properties. Organic compounds are studied as a separate branch of chemistry because of the following reasons:

- Existence of innumerable organic compounds.
- Properties of organic compounds are distinctly different from those of inorganic compounds.

The different between organic and inorganic compounds are summarised below.

	ORGANIC COMPOUNDS	INORGANIC COMPOUNDS
Composition	1. Usually contain carbon, especially carbon-hydrogen bonds. 2. Composed of few elements only, commonly carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorous.	1. May contain carbon. Usually contain metal and other elements. Does not contain carbon-hydrogen bonds. 2. Composed of all the known elements.
Source	Generally found in living matter, i.e., animals and plants.	Generally obtained from non-living matter, i.e., minerals.
Nature	Biological in nature	Mineral in nature
Physical state	Many are gases, liquids or solids	Most are solids
Number	Many	Fewer
Isomerism	Exhibit the phenomenon of isomerism.	Only the complex compounds show the phenomenon of isomerism.
Homologous series	Classified into many classes on the basis of functional groups, known as homologous series.	Classified as acids, bases and salts. No homologous series found.
Size	Some compounds are extremely large with large molecular masses. These large compounds are stable.	Are generally small. Comparatively large compounds are generally less stable.
Flammability	Highly inflammable due to their readiness of undergoing combustion in oxygen.	Not inflammable as they are not combusting in oxygen readily.
Type of bond	Form covalent	Most form ionic. Some are covalent.
Salt formation	Unable to make salts due to the covalence of carbon.	Make salts
Thermal stability	Less stable	More stable
Conduction	Poorer conductors of heat and electricity in aqueous solutions.	Better conductors of heat and electricity in aqueous solutions.
Rate of reaction	Slow	Fast
Solubility	Insoluble in water, soluble in organic solvents.	Soluble in water, insoluble in organic solvents.

CLASSIFICATION OF ORGANIC COMPOUNDS

There are millions of organic compounds and this makes it impossible to study each individual compound. To facilitate their study, organic compounds are classified into various groups and sub-groups.

- They may be broadly classified into the following classes:

- Aliphatic compounds
- Cyclic compounds

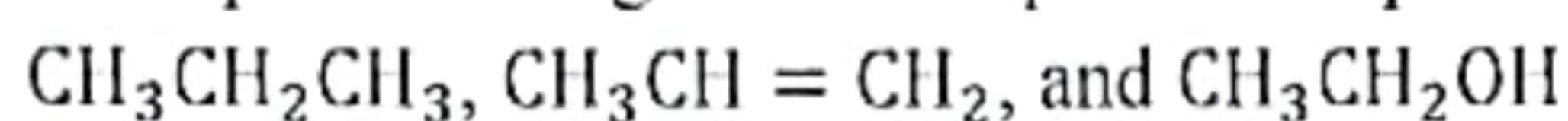
Aliphatic compounds

These are organic compounds with open carbon chain structure.

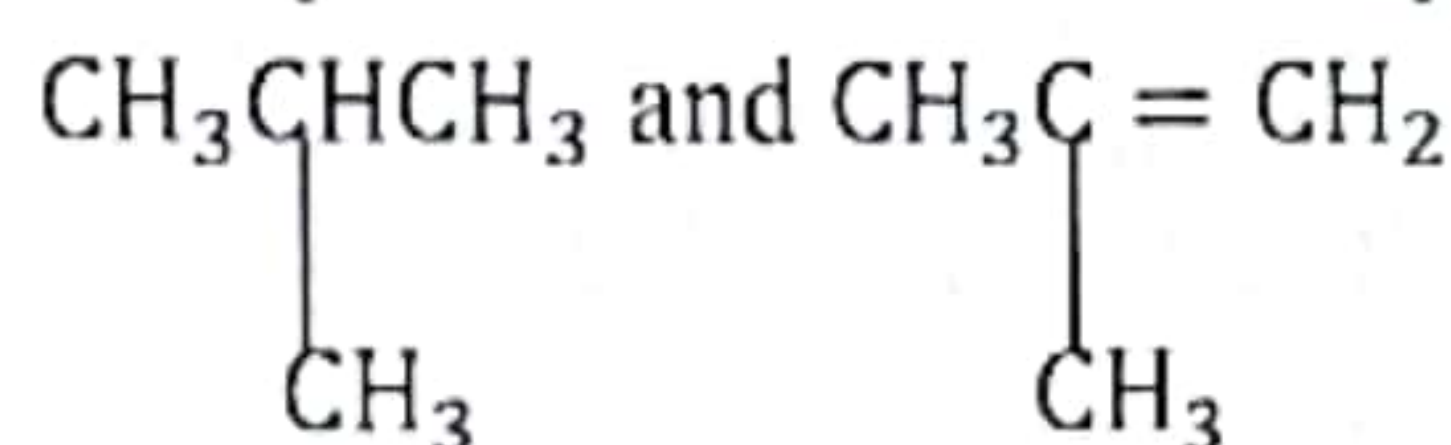
- The chain may be branched or straight
- It may contain single, double, triple bonds or any combination of the three.

Aliphatic compounds are also known as **acyclic compounds**.

- Examples of straight chain aliphatic compounds are:



- Examples of branched chain aliphatic compounds are:



Cyclic organic compounds

These are organic compounds with closed carbon chain structure.

- The structure may be branched or straight
- It may contain single, double, triple bonds or any combination of the three.

Cyclic compounds are also known as **ring compounds**.

- They can further be divided into:
 - Homocyclic compounds
 - Heterocyclic compounds

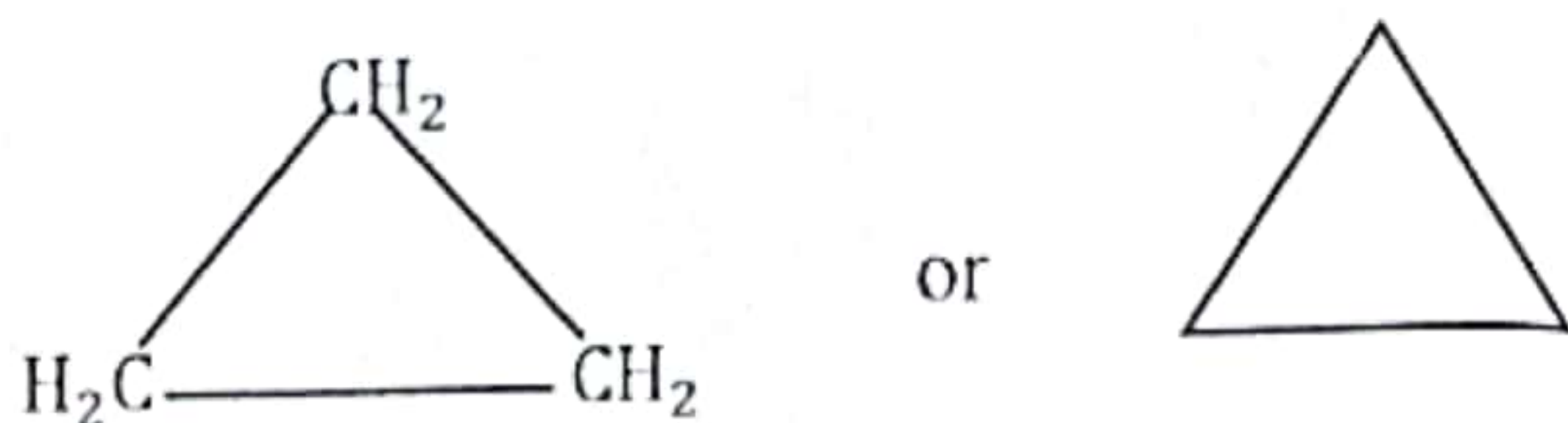
Homocyclic compounds

These are compounds in which the ring consists of only carbon atoms.

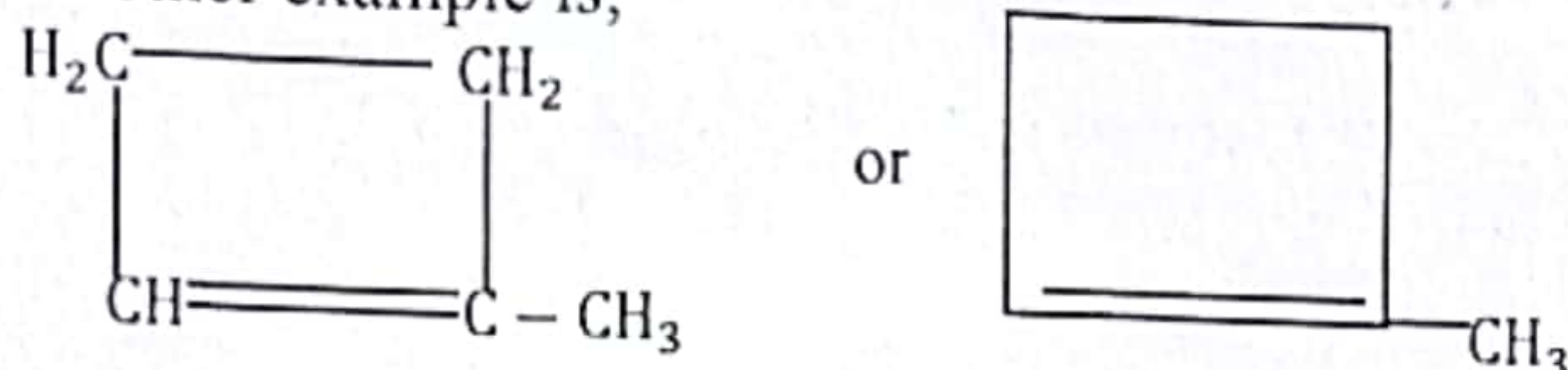
- They are also known as **carbocyclic compounds**.

Homocyclic are further divided into **alicyclic** and **aromatic compounds**.

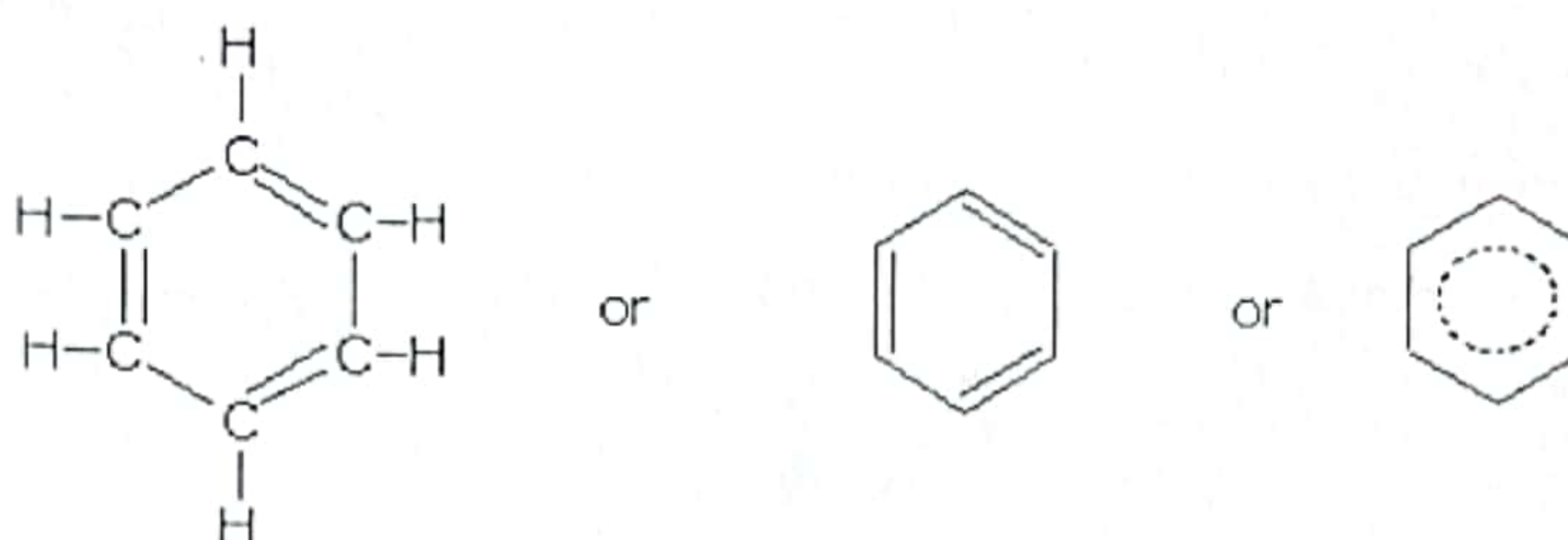
- **Alicyclic compounds** are formed when a ring of three or more carbon atoms resembling aliphatic compounds are contained in homocyclic compounds. For example:



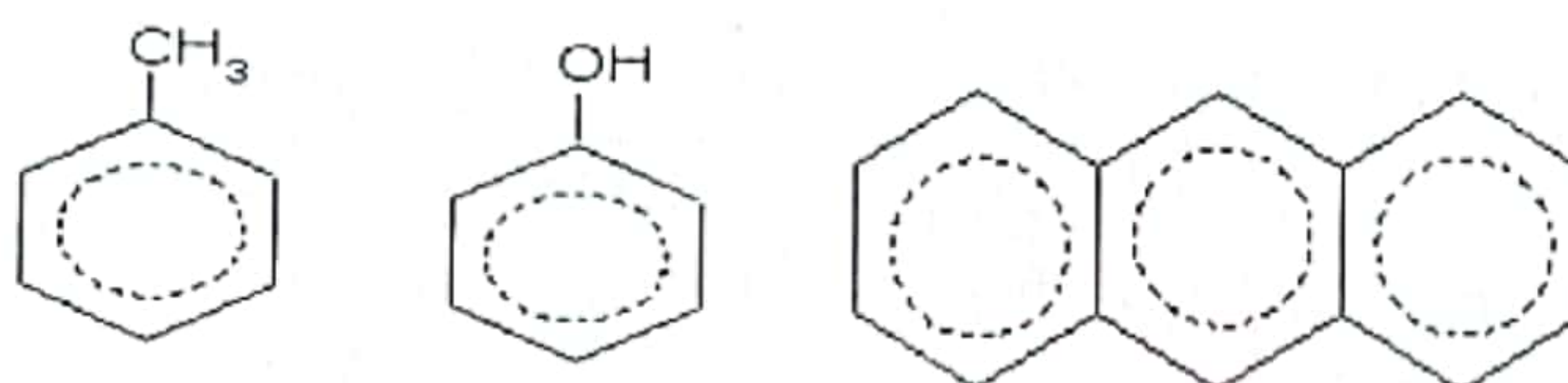
Another example is;



- **Aromatic compounds** are *homocyclic compounds which contain at least one benzene ring*. Whereas benzene ring consists of six carbons atoms with alternate double and single bonds as shown below.



- Examples of aromatic compounds are:



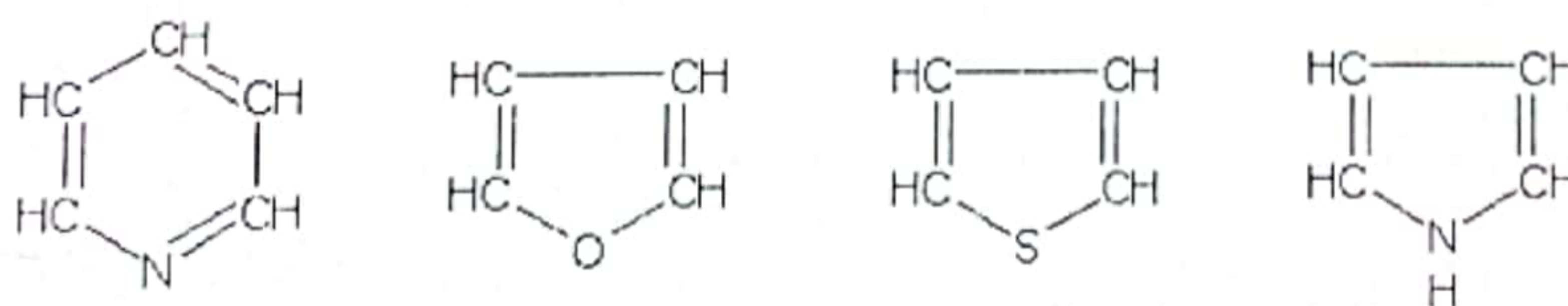
Heterocyclic organic compounds

These are *cyclic compounds which are formed when atoms of more than one kind make up the ring in the compounds*.

- In these compounds generally one or more atoms of elements, in most cases nitrogen, oxygen, or sulphur are present.

The atom other than that of carbon (i.e. N, O or S) present in the ring is called **hetero atom**.

- Examples of heterocyclic compounds are:



CLASSIFICATION OF CARBONS IN ORGANIC COMPOUNDS

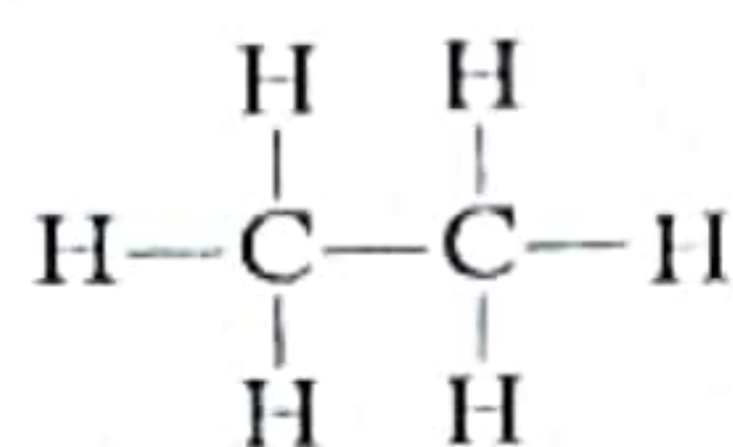
Carbons in the organic compounds with two or more carbons may be classified as:

- Primary (1°) carbon
- Secondary (2°) carbon
- Tertiary (3°) carbon
- Quaternary (4°) carbon

Primary carbon

Primary carbon is the carbon that is directly bonded to one carbon only.

- For example **both of the carbons** in the compound below are primary.

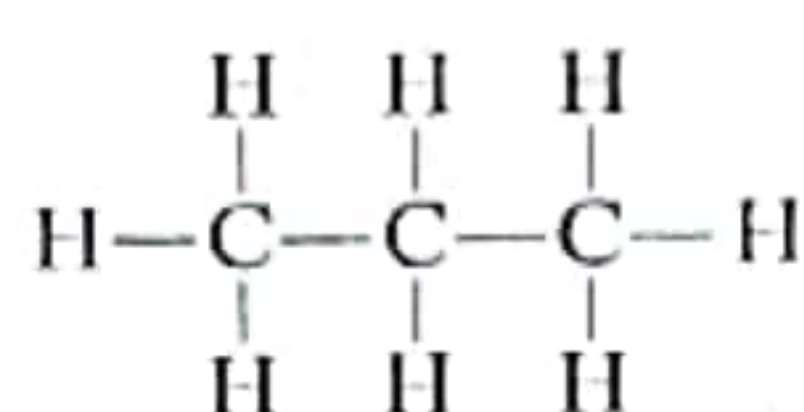


- *Hydrogen bonded to primary carbon* is known as **primary hydrogen**.

Secondary carbon

Secondary carbon is the carbon bonded to two other carbons.

- For example the **second carbon (at the centre)** is the only secondary carbon in the compound below.

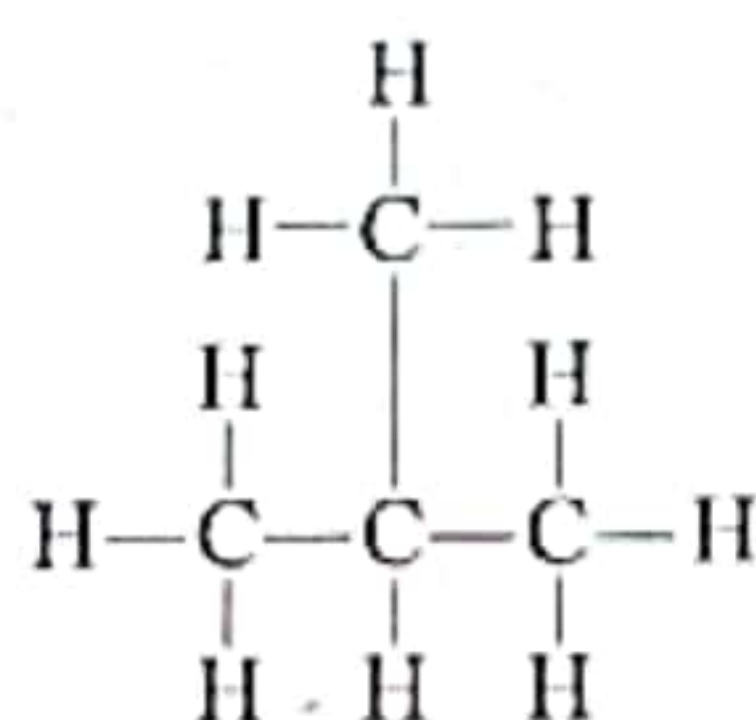


- *Hydrogen bonded to secondary carbon* is known as **secondary hydrogen**.

Tertiary carbon

Tertiary carbon is the carbon bonded to three other carbons.

- Again the second carbon at the centre in the compound below is the tertiary carbon.

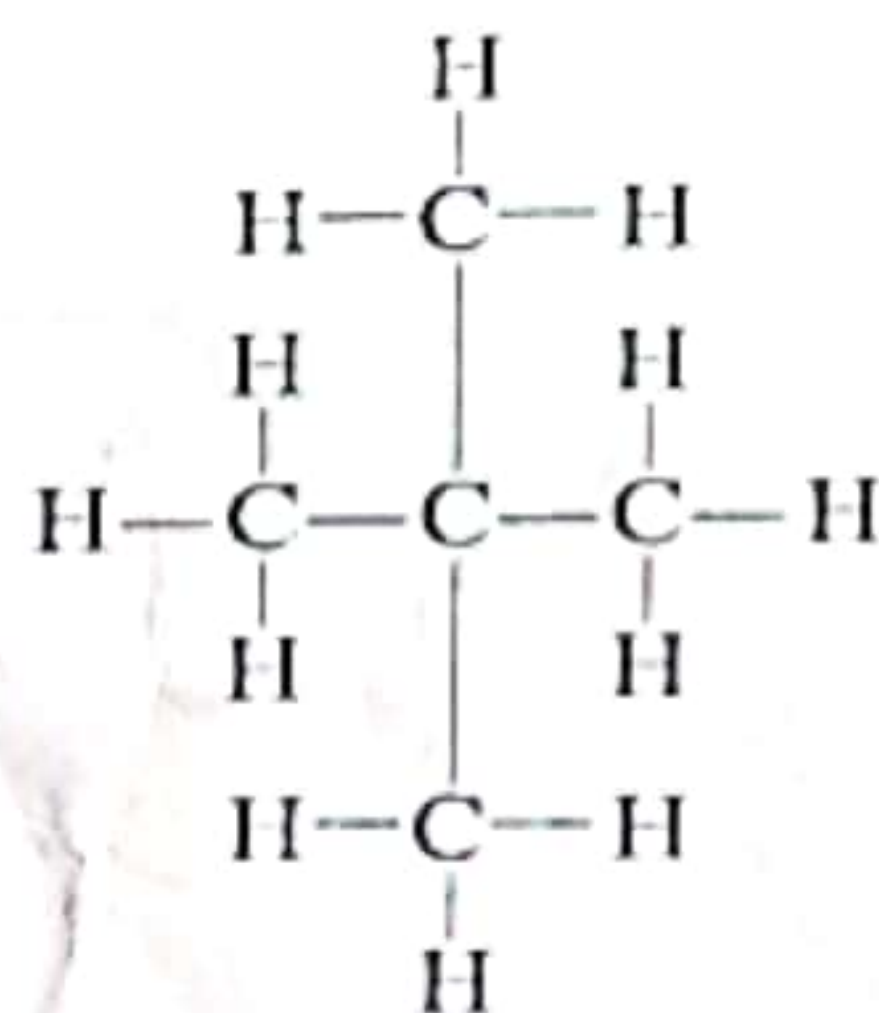


- *Hydrogen bonded to tertiary carbon* is known as **tertiary hydrogen**.

Quaternary carbon

Quaternary carbon is the carbon bonded to four other carbons.

- Again the second carbon at the centre in the compound below is the quaternary carbon.



- Because all of its valencies are consumed in bonding to other carbons, a quaternary carbon can not be bonded to hydrogen and hence quaternary hydrogens do not exist.

PRACTICE EXERCISE 1

Problem 1

"Organic compounds are said to contain vital force" By considering source of organic compounds, briefly support and oppose this statement.

Problem 2

There are millions of organic compounds while only fewer inorganic compounds are known. Justify.

Problem 3

Chemists had decided to study organic compounds as a separate branch of chemistry. Give two reasons to support this decision.

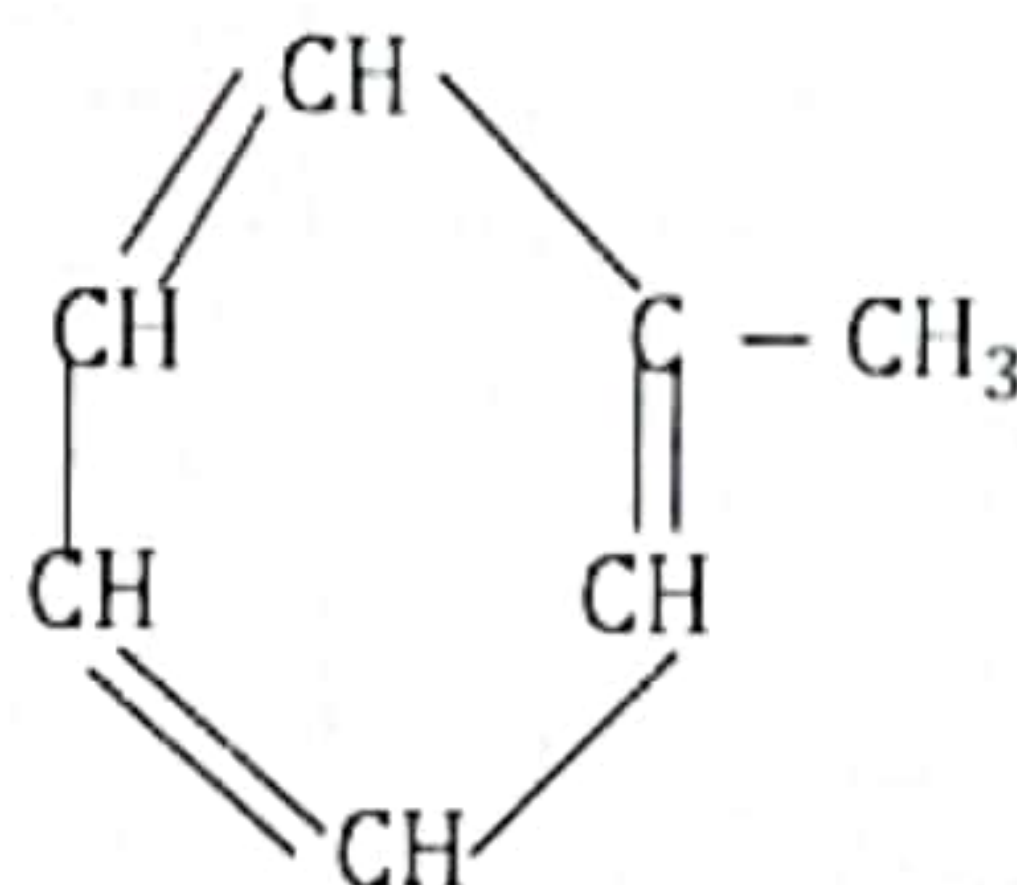
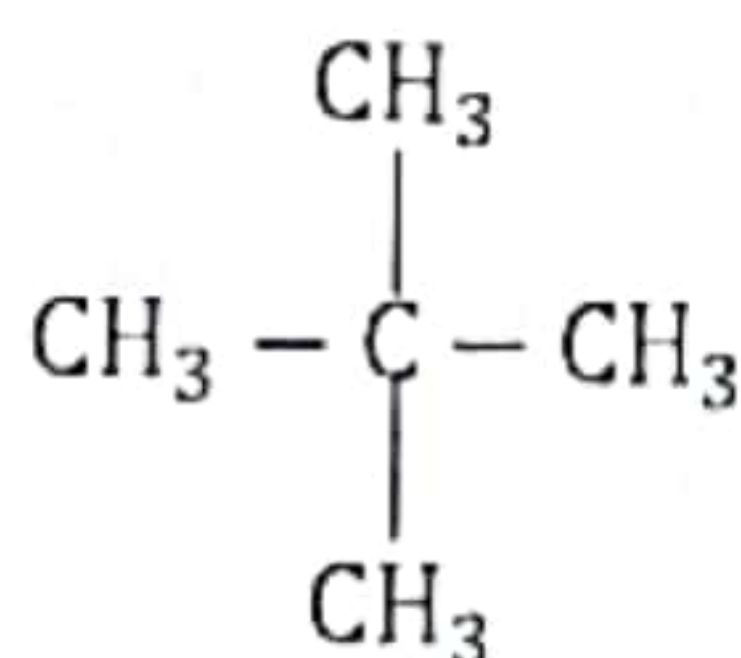
Problem 4

List down differences between organic and inorganic compounds based on their:

- Composition
- Source
- Type of bond
- Flammability
- Conduction

Problem 5

Classify the following organic compounds whether is aliphatic, homocyclic, heterocyclic or aromatic.



Chapter 2

ORGANIC REACTANTS

Organic reactant is any specie capable of taking part in organic reaction.

- Important thing to note about organic reactant is that for specie to be an organic reactant, not necessary for the substance to be organic. Compounds like AlCl_3 and H_2SO_4 are inorganic but are also termed as organic reactant because they can participate in organic reaction.

Usually a substance can undergo chemical reaction if either it has deficiency of electrons so that it can accept electrons during the chemical reaction or it has excess of electrons so that it can supply electrons during the chemical reactions.

- According to ability of supplying or accepting electrons, organic reactants can be grouped into three types namely;
 - Nucleophile (Nu^-)
 - Electrophile (E^+)
 - Free radical (R)

NUCLEOPHILE

The word **nucleophile** originates from two words: 'nucleus' and Greek word 'philo' which means love.

- So literally, nucleophiles are nuclear loving species. Are positive charges lovers.

By definition:

Nucleophile is electron-rich specie with tendency to donate an electron pair to electron-poor specie (called electrophile) to form new covalent bond.

- Nucleophiles can further be divided into three types.

(i) Substance with net negative charge

Substances with have negative charges have excess electrons to donate to electron deficient species thus acting as nucleophile. Examples of nucleophiles which fall under this category are: HO^- , CN^- , RO^- , and X^- where R and X^- stands for alkyl group and halogen respectively.

(ii) Substance with at least one atom possessing lone pair in its electronic structure (Lewis base)

Lone pair is valence electrons of an atom which do not take part in the bond formation.

- So those electrons which would take part in the bond formation can be donated to deficient species during the reaction hence the substance acts as a nucleophile. Examples of nucleophiles under this category are water, H_2O , and ammonia, NH_3 .

The reader should understand that:

- In any neutral molecule containing oxygen like in ROH there is always two lone pairs in the oxygen atom.
- In any neutral molecule containing nitrogen like in RNH_2 there is always one lone pair in the nitrogen atom.

(iii) Molecule with pi (π) bond in its structure

Pi bond is weak because it is formed by sideways overlapping of atomic orbitals which has small region of overlapping of atomic orbitals. Also pi bond cannot exist in its own without presence of sigma bond which is stronger (i.e. π bond present in double or triple bond).

- So pi electrons can be donated to deficient species and the molecule becomes nucleophile. Good examples of nucleophiles under this category are alkenes with $C = C$ and alkynes with $C \equiv C$.

Factors affecting nucleophilicity

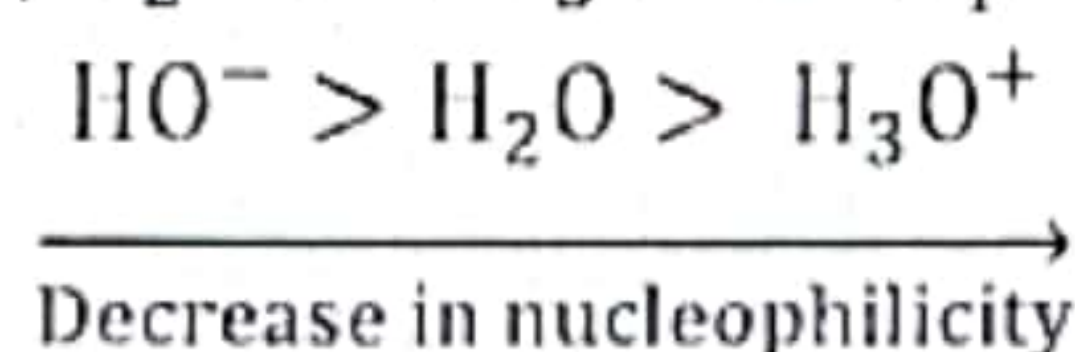
Nucleophilicity or nucleophile strength is the relative reactivity of a nucleophilic reagent. It refers to a substance's nucleophilic character. It is sometimes termed as **nucleophilic power**.

- There are various factors affecting reactivity of nucleophiles including the following:
 - Negative charge intensity
 - Electronegativity
 - Atomic size
 - Nature of the solvent of reaction medium

Negative charge intensity

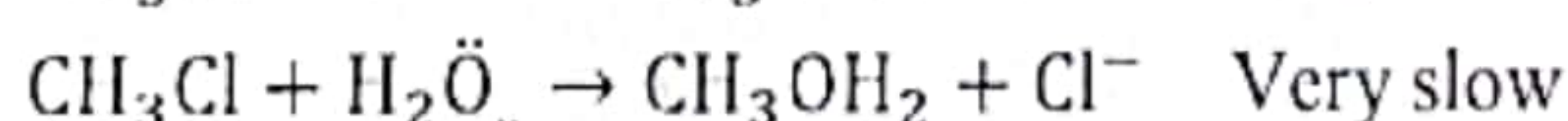
It has been experimentally shown that a nucleophile containing a negatively charged reactive atom is better than a nucleophile containing a reactive atom that is neutral.

- So nucleophilicity increases as the charge on the atom become more negative. For example nucleophilicity of HO^- , H_2O and H_3O^+ is expected to follow the following trend:

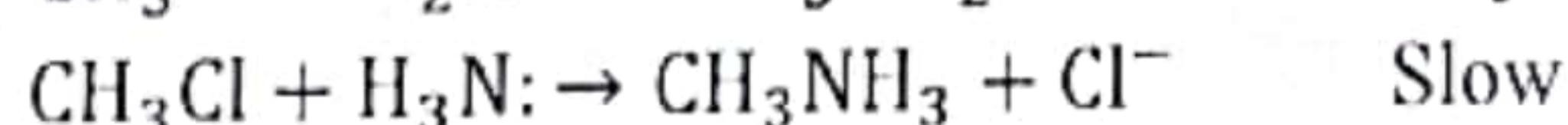
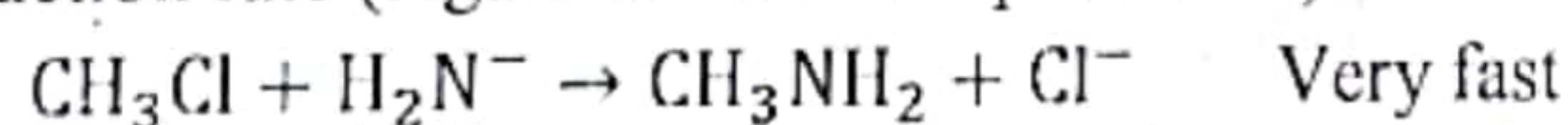


Therefore:

- The O of HO^- is a better nucleophile than the O of H_2O , and results in a faster reaction rate (See an example below which involve substitution of nucleophiles)



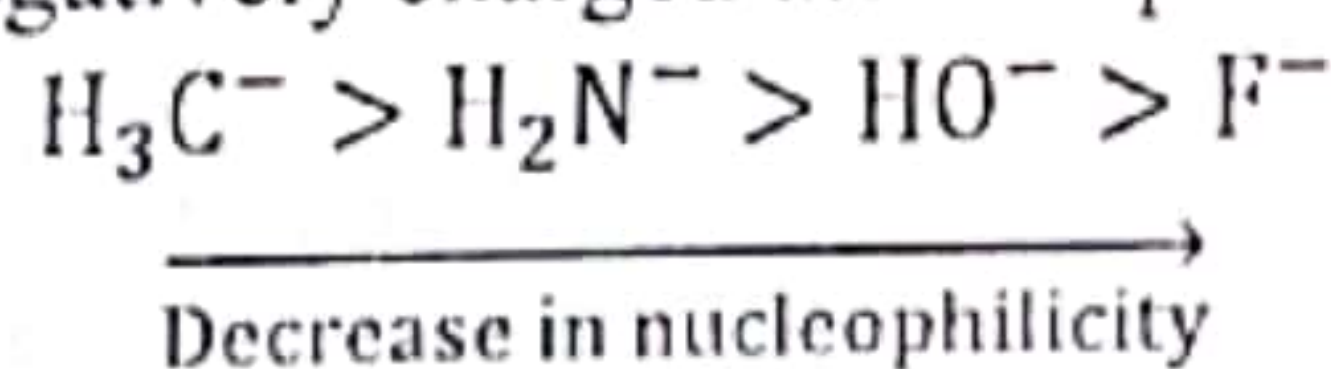
- Similarly, when nitrogen is part of NH_2^- , it has a negative charge, and when it is part of NH_3 , it is neutral. Therefore, the N of NH_2^- is a better nucleophile than the N of NH_3 , and results in a faster reaction rate (Again see an example below).



Electronegativity

Electronegativity provides good explanation for variation of nucleophilicity as you across the period (from left to right) of modern periodic table.

- Like in the case of basicity where basic strength across the period decreases as the electronegativity increases, nucleophilicity decreases in the same order by the same reasoning. Generally it can be concluded that **in most cases nucleophilicity increases as basicity increases**. For example nucleophilicity of negatively charged atom of period 2 follows the following order:



Atomic size

Size of reactive atom in the nucleophile and hence size of nucleophile is dominant factor in explaining the variation of nucleophilicity of neutral (uncharged) nucleophiles in descending groups of the periodic table.

- The nucleophilicity is found to increase as size increases in descending the group because larger nucleophiles have more diffuse, and more polarisable electron clouds as the electrons become more weakly held by nuclear attractive force as the size increases.

For example S being below O in the periodic table its hydride, H_2S , has larger size than H_2O (hydride of O) and hence H_2S become stronger nucleophile. Another example; PH_3 is stronger nucleophile than NH_3 for similar reasoning although NH_3 is more basic in character than PH_3 .

Nature of solvent of reaction medium

Solvents can be classified as being either **polar** or **non-polar**. Polar solvents can be further subdivided into **protic** and **aprotic** solvents.

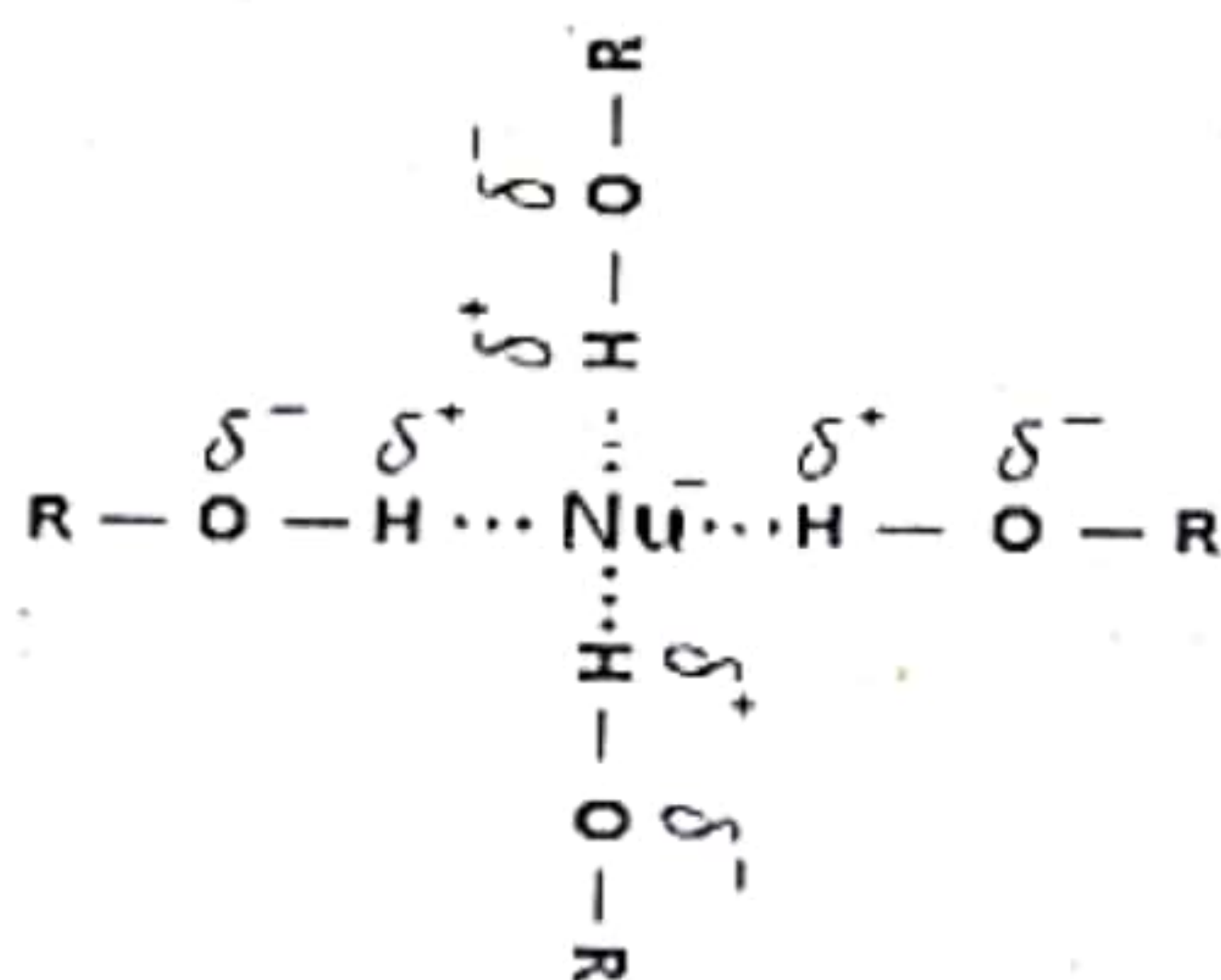
- A **protic solvent** is a solvent that has a hydrogen atom bound to an oxygen or nitrogen. So **protic solvents** have **positively polarised hydrogen atom**. Examples of protic solvents include H_2O , ROH and RNH_2 (Where water is an example of an inorganic protic solvent, and alcohols and amines are examples of organic protic solvents).
- An **aprotic solvent** is a solvent that lacks positively polarised hydrogen. Examples of aprotic solvent are CH_3COCH_3 and CH_3CN .

What happen when nucleophile is in polar protic solvent?

When protic solvents are used as medium in nucleophilic reactions, the positively polarised hydrogen of the solvent molecule can interact with the negatively charged nucleophile through **hydrogen bonding**.

- In solution, molecules or ions that are surrounded by these solvent molecules are said to be **solvated**. **Solvation** is the process of attraction and association of solvent molecules with ions of a solute. The solute, in this case, is a negatively charged nucleophile.

In the case below, we are using an alcohol (ROH) as an illustration of a nucleophile in protic solvent, but be aware that this interaction can occur with other solvents containing a positively polarised hydrogen atom, such as a molecule of water or amines.



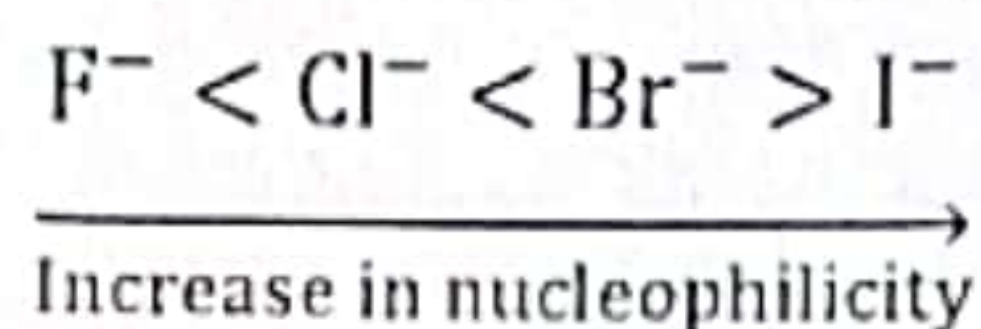
Nucleophile in the protic solvent

What effect of this solvation?

Solvation weakens the nucleophile; that is, solvation decreases nucleophilicity. This is because the solvent forms a "shell" around the nucleophile, decreasing the nucleophile's ability to attack electron deficient specie (**electrophile**).

- Furthermore, because the charge on smaller anions is more concentrated, **small anions** are more **tightly solvated** than **large anions** and hence they become **less nucleophilic** as their lone pairs become less accessible to electrophile as result of the solvation.

The decrease of solvation (through hydrogen bonding between protic solvent and halide ions) as result of increase in anionic radii explains why nucleophilic strength of halides decreases in descending the halogen group.



What about polar aprotic solvent?

Aprotic solvents, like protic solvents, are polar but, because they lack positively polarised hydrogen, they do not form hydrogen bonds with the anionic nucleophile.

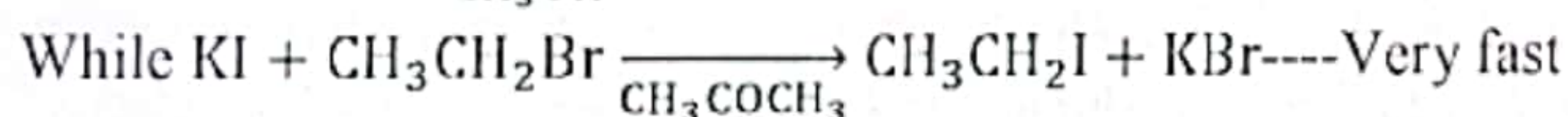
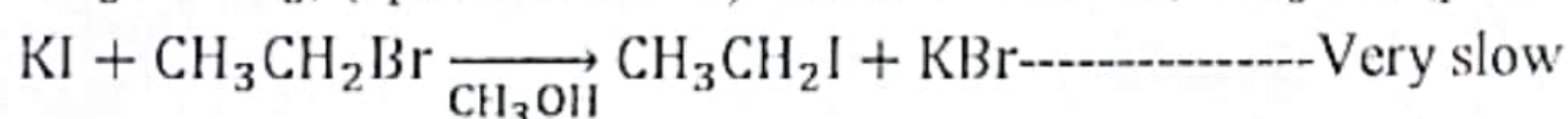
- This results to weak solvation as result of relatively weak interaction between the aprotic solvent and the nucleophile.

There are two important effect of this weakened interaction.

First effect:

By using an aprotic solvent as reaction medium, the reactivity of the nucleophile is increases.

- This increases the rate of reaction of which is nucleophile is main reactant.
- For example, the reaction between bromoethane and potassium iodide, occurs faster in acetone, CH_3COCH_3 , (aprotic solvent) than in methanol, CH_3OH , (protic solvent).



Second effect

A second effect that results from the weak interaction that occurs between aprotic solvents and nucleophiles is that, under some conditions, there can be a reverse of the reactivity order.

- The reverse would result in nucleophilicity following trend of basic strength in going down and up the group.
- For example in protic solvents, the iodide anion is the strongest nucleophile while in aprotic solvents under some conditions; the fluoride anion being strongest base among halides is the strongest nucleophile.

ELECTROPHILES

The word **electrophile** originates from two words: 'electron' and Greek word 'philo' which means love.

- So literally, electrophiles are electron loving species.

By definition:

Electrophile is electron-poor specie with tendency to accept an electron pair from electron-rich specie (called nucleophile) to form new covalent bond.

- So always there is chemical reaction between nucleophile (donates a pair of electrons) and electrophile (accepts a pair of electrons)

Electrophiles can further be divided into two types:

- (i) **Substance with net positive charge (charged electrophiles)**
Substances with positive charge have deficiency of electrons, so they can accept electrons during the organic reaction thus acting as electrophiles. For example; H_3C^+ and $(\text{CH}_3)_3\text{C}^+$ are electrophiles falling under this category.
- (ii) **Lewis acid (uncharged electrophiles)**

Lewis acid is an electron acceptor.

- Compounds like AlCl_3 and BF_3 having empty orbitals in their electronic structure, they can accept pair of electrons from Lewis base thus acting as Lewis acid. Being able to accept a pair of electrons those compounds are electrophiles too.

Lewis acids always are used as catalysts in electrophilic substitution reaction in aromatic compounds.

FREE RADICALS

Free radicals or simply **radicals** are chemical species (atom or group of atoms) which have a single unpaired electron.

- So free radicals are highly unstable and they lack only one electron to attain stability of full filled electronic structure and hence they are very reactive.

To show that a species (either an atom or a group of atoms) is a free radical, the symbol is written with a dot attached to show the unpaired electron. For example:

- Chlorine radical, $\text{Cl}^\bullet$
- Methyl radical, $\text{H}_3\text{C}^\bullet$

It should be noted that:

- There is no chemical reaction between free radical and nucleophile because free radical needs one electron only in the reaction while nucleophiles donate a pair of electrons (two electrons).
- Also there is no chemical reaction between electrophile and free radical because electrophile does not donate electron (while free radical need one electron). So.....!

Free radical reacts with another free radical.

PRACTICE EXERCISE 2

Problem 1

Izanga is a form five student studying PCB combination at Hopegen secondary school. In the chemistry test, Izanga failed to give correct definition of three terms: nucleophile, electrophile and free radical. Below are definitions of the terms as attempted by Izanga in the test:

- i. **Nucleophile:** Is the electron-rich specie with tendency to donate electron specie to form new covalent bond.
- ii. **Electrophile:** Is the electron-poor specie with tendency to accept an electron pair from electron-rich specie to form new covalent bond.
- iii. **Free radical:** is the chemical specie which has a single unpaired electron such that can accept an electron pair to form new covalent bond.

If Izanga would need your help in doing correction, explain how you would help him by doing the following:

- i. Telling him what is wrong with his definition
- ii. Giving correct definition

Problem 2

By giving reason(s) support or oppose each of the following:

- i. All nucleophiles have lone pair
- ii. All electrophiles have empty orbital
- iii. The bond formed between nucleophile and electrophile is always dative bond
- iv. Free radical may combine with nucleophile to form covalent bond
- v. BF_3 is stronger nucleophile than AlCl_3

Problem 3

Arrange the following species in order of increasing their nucleophilicity

- i. Br^- , Cl^- , I^- , F^-
- ii. F^- , H_2N^- , H_3C^- , HO^-
- iii. H_2O , HO^- , H_3O^+ ,

Problem 4

Compare electrophilicity of charged electrophiles and uncharged electrophiles.

Problem 5

If you want to prepare $\text{CH}_3\text{CH}_2\text{I}$ by the reaction between $\text{CH}_3\text{CH}_2\text{Br}$ and KI , would you use CH_3OH or CH_3COCH_3 as solvent medium? Give reason for your choice.

Chapter 3

ORGANIC REACTIONS MECHANISM

A reaction mechanism is the sequence of steps which occurs in the chemical reaction.

- It is a step-by-step description of the order in which bonds break and atoms rearrange during a reaction.

Studying reaction mechanisms help us to:

- Make sense of (i.e. see patterns in) the reactions;
- Change the experimental conditions under in order to increase the yield of products; and
- Predict what might happen in a reaction.

TYPES OF BOND CLEAVAGE MECHANISM

There are two types of bond cleavage (breaking or fission) mechanism which are:

- Homolytic bond cleavage and
- Heterolytic bond cleavage

Homolytic bond cleavage

Homolytic bond cleavage or homolysis is the type of bond cleavage mechanism whereby two bonding electrons split equally between bonding atoms by each atom taking one electron from bonding electrons.

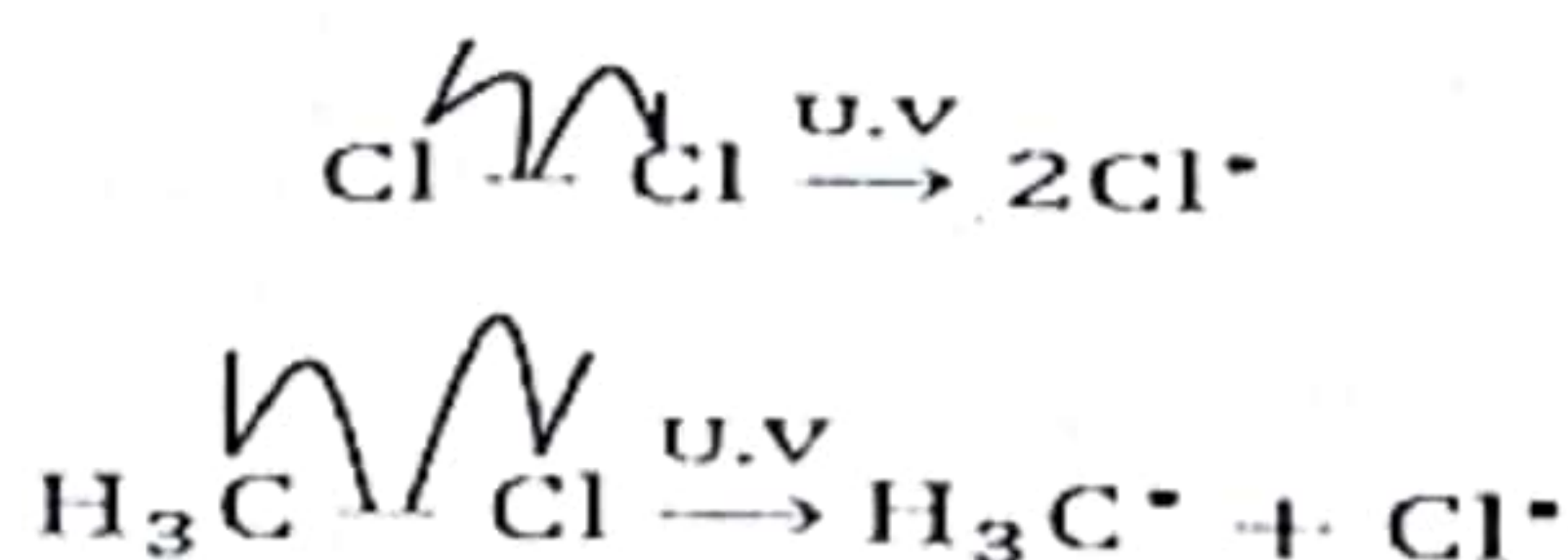
- Since each bonded atom takes its own electron resulting to a single unpaired electron in each, homolytic bond cleavage leads to formation of free radicals hence the term **radical cleavage** for homolytic bond cleavage.

Homolytic bond cleavage is initiated by presence of at least one of the following conditions:

- Ultra violet light (U.V)
- Very high temperature (above 500°C)
- Organic peroxide like RO – OR or RCO – O – O – COR
- Gaseous state of reactant or non-polar solvent as reaction medium
- Electricity (high voltage)

Homolytic bond cleavage is shown by using a half headed curved arrow (↷)

-For example:



Mechanism of the reaction in which homolysis takes place is known as **homolytic mechanism** or **free radical mechanism**.

Heterolytic bond cleavage

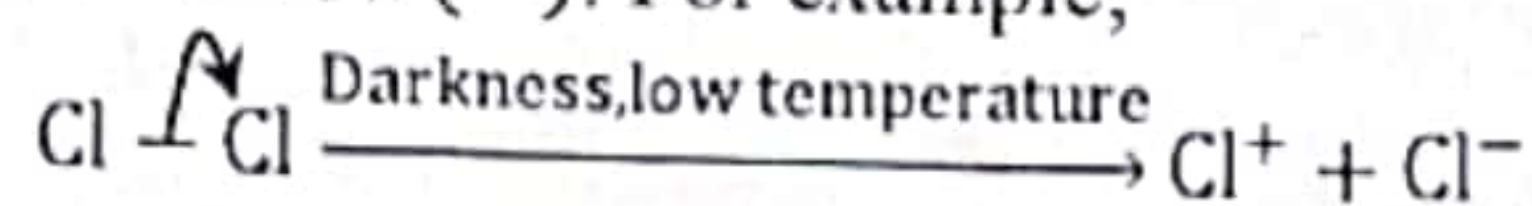
Heterolytic bond cleavage or heterolysis is the bond cleavage mechanism whereby one bonded atom takes all two bonding electrons in the cleavage. It is also known as **polar cleavage**.

- The atom which take all bonding electrons become negatively charged and that one which is deprived with electrons become positively charged.

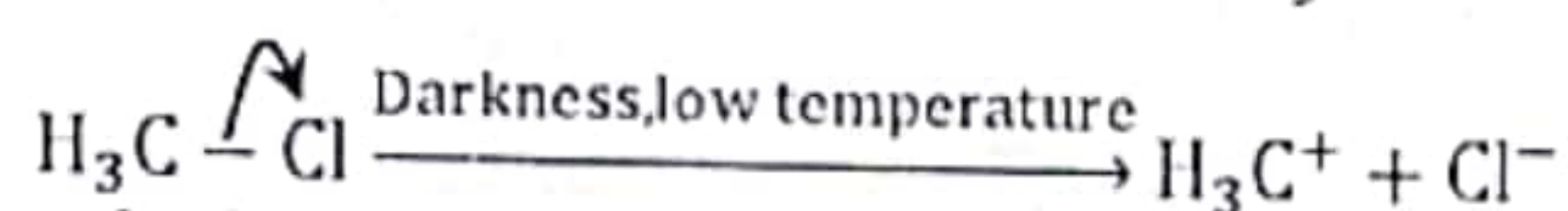
- So heterolytic bond cleavage leads to formation of nucleophile and electrophile.

Heterolytic bond cleavage occurs in all conditions which do not favour homolytic bond cleavage.

- It is shown by full headed curved arrow ($\curvearrowright$). For example;



If the bond comprises atoms of different elements, then the atom which is more electronegative takes the electrons. For example for a bond which comprises carbon and chlorine; chlorine being more electronegative must take all two bonding electrons in the heterolysis.



Mechanism of the reaction in which heterolysis takes place is known as **heterolytic mechanism** or **ionic mechanism**.

RULES OF SHOWING REACTION MECHANISM IN ORGANIC REACTION

The following simple rules enable to show reaction mechanism in organic reactions.

Rule 1

To show movement of electron(s), headed curved (or curly) arrow is used. The tail of the arrow should start at the source of electrons and the head should direct to the site where electrons are going to be kept (i.e. the head should direct to the electron sink).

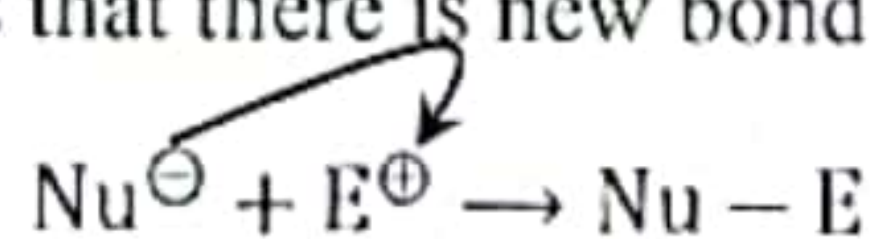
- Nucleophiles and bonding sites are source of electrons.

Rule 2

To show movement of one electron a half headed curved arrow ($\curvearrowleft$) is used and to show movement of an electron pair (two electrons) a full headed curved arrow ($\curvearrowright$) is used.

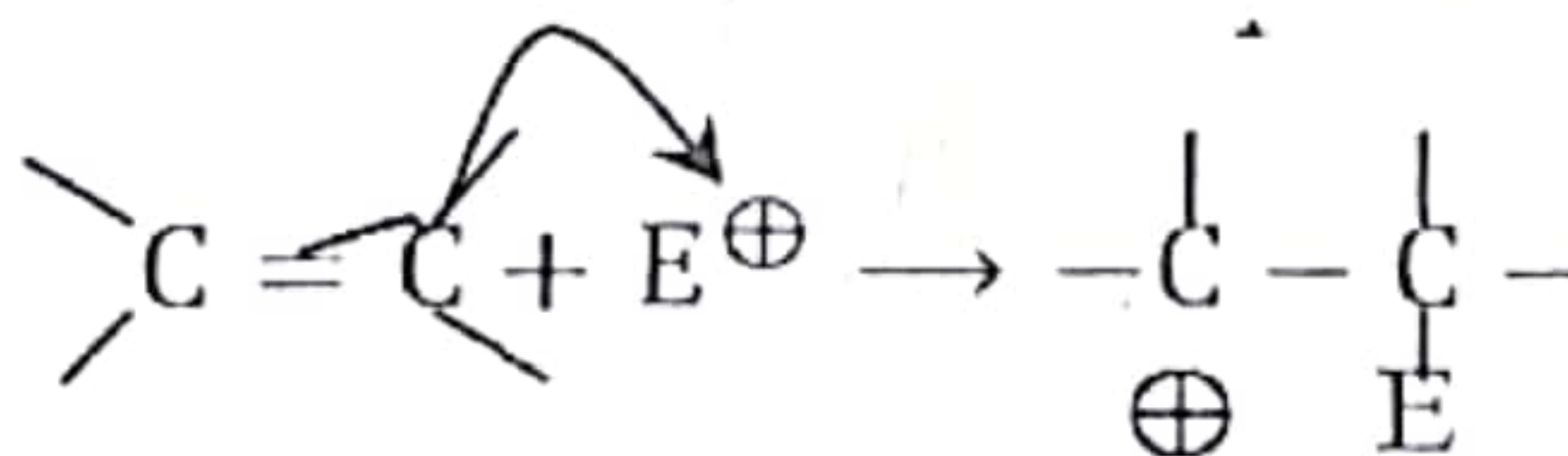
Rule 3

If there is movement of an electron pair from nucleophile to the electrophile (i.e. an arrow starts from nucleophile to electrophile), it indicates that there is new bond which is formed between them.

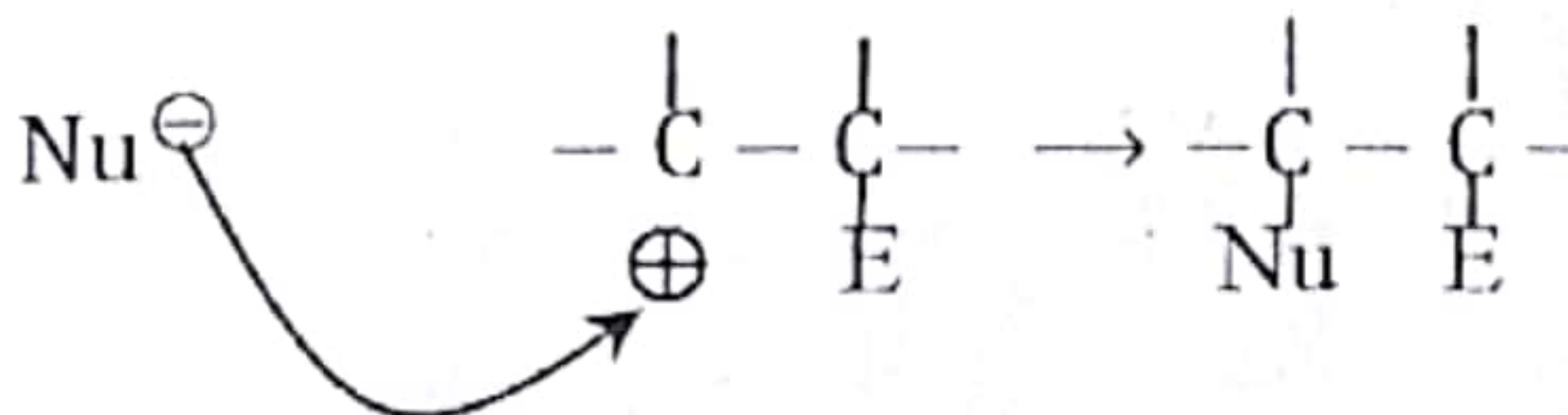


Rule 4

If a molecule acts as nucleophile by using π bond, an arrow must pass through the carbon where a new bond will be formed and the remaining carbon which originally had π bond becomes positively charged.



The positive charge on the carbon is neutralised by joining the carbon with Nu^- .



Rule 5

If a molecule acts as a nucleophile by using lone pair then the atom which donates its lone pair electrons becomes positively charged.

The positive charge which is formed on the atom cannot be neutralised by combining with nucleophile, why?

Because any atom which reaches the extent of donating its lone pair has already attained stable structure of noble gas (i.e. octet structure with 8 electrons in its valence shell) so combining with another nucleophile makes it to have 10 electrons in its valence shell which is against octet rule hence it is impossible.

So....! How the positive charge is neutralised?

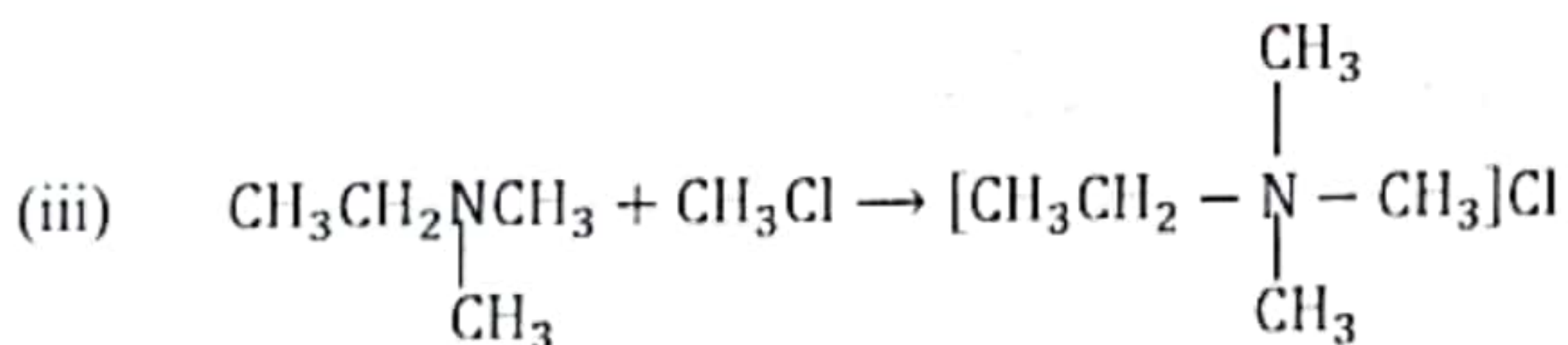
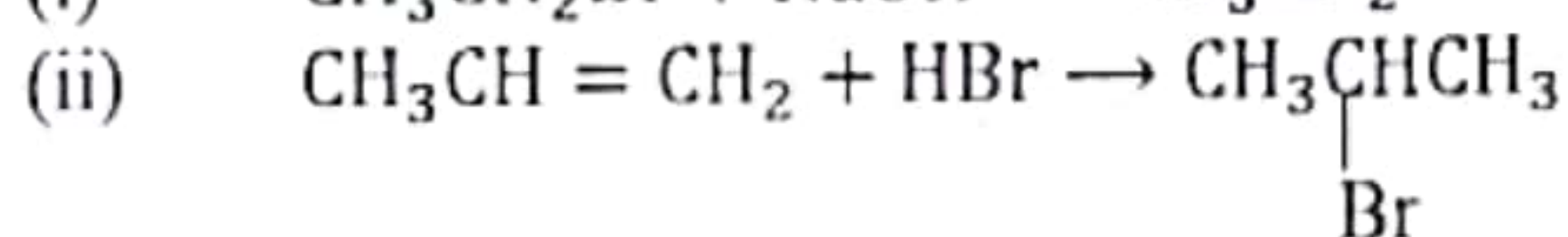
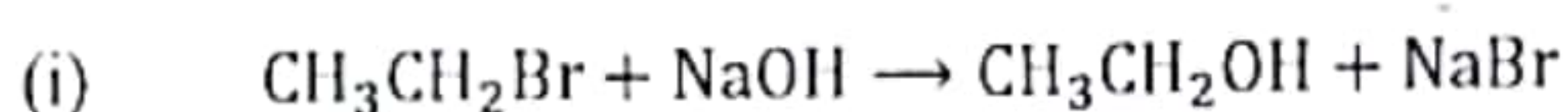
The positive charge is neutralised by breaking one of the bonds originally present in the atom which donates its lone pair electrons and the bond must be different to the new bond which is formed.

What if bonds are all alike?

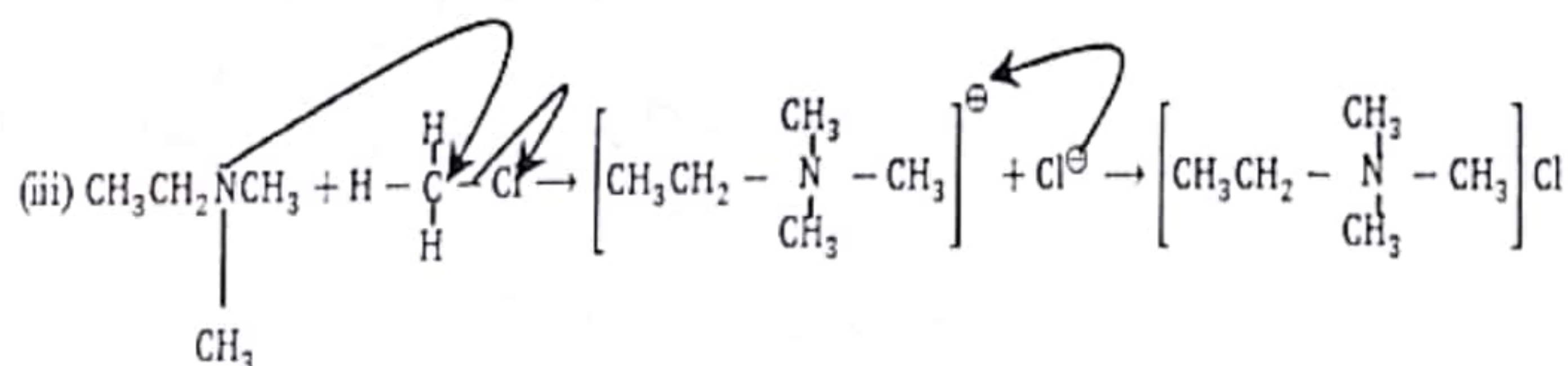
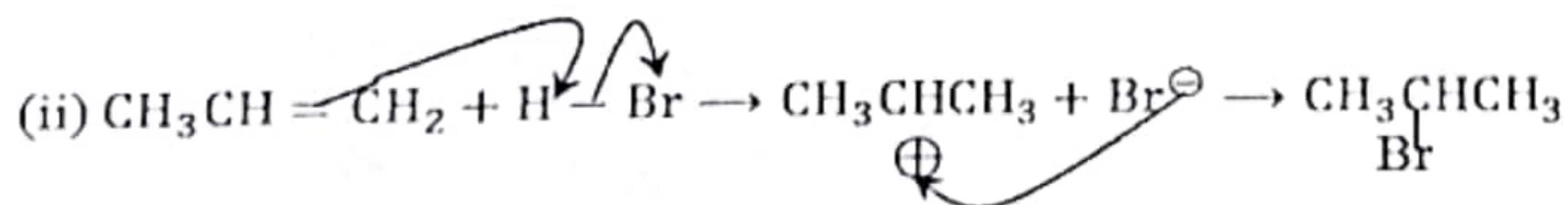
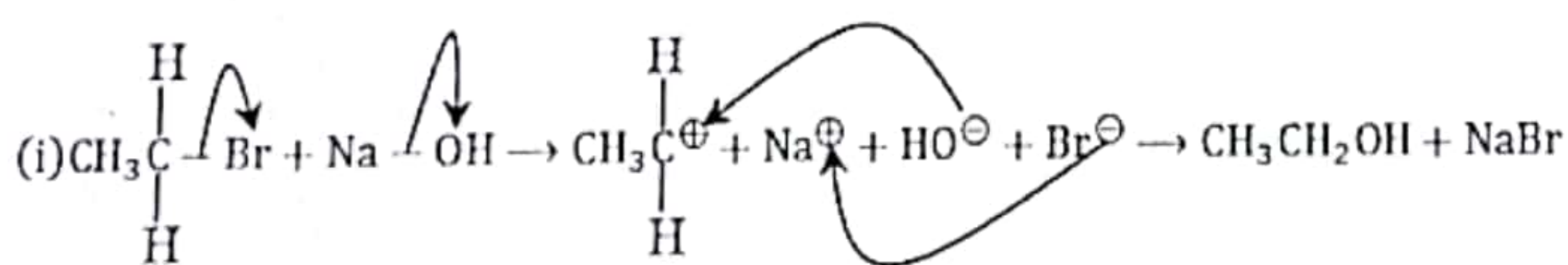
If all bonds are the same, the positive charge is delocalized and the whole molecule becomes positive charge.

Example 1

Show reaction mechanism of the following organic reactions



Solution

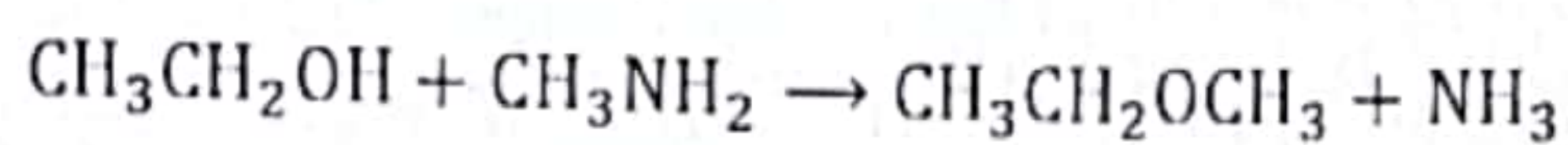


It should be noted that:

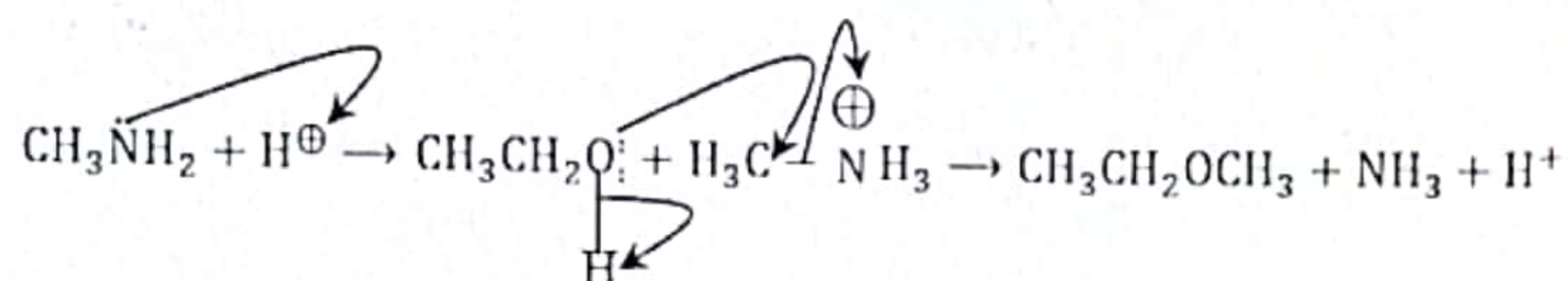
There is no chemical reaction between two nucleophiles unless there is acidic medium which initiates the reaction (see example 2 below).

Example 2

Show reaction mechanism of the following organic reaction



Solution



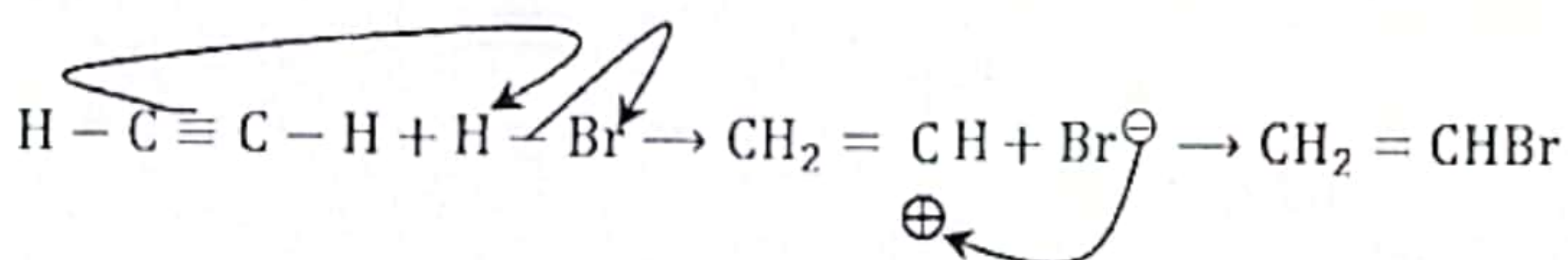
Example 3

Show reaction mechanism of the following organic reaction;

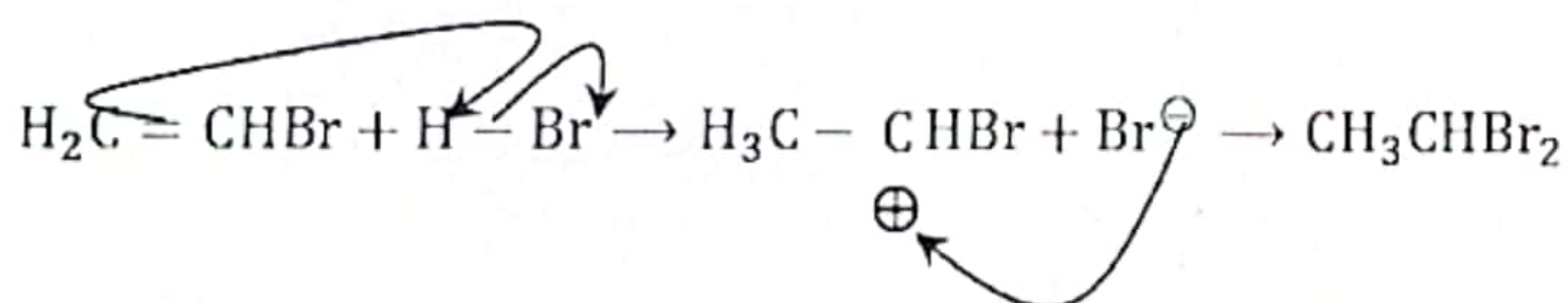


Solution

Addition of first molecule of HBr



Addition of second molecule of HBr



PRACTICE EXERCISE 3

Problem 1

- What is the reaction mechanism?
- What are significances of studying reaction mechanism?

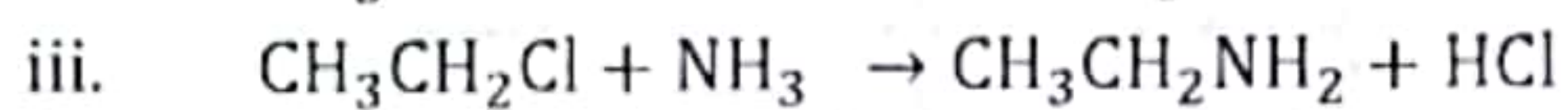
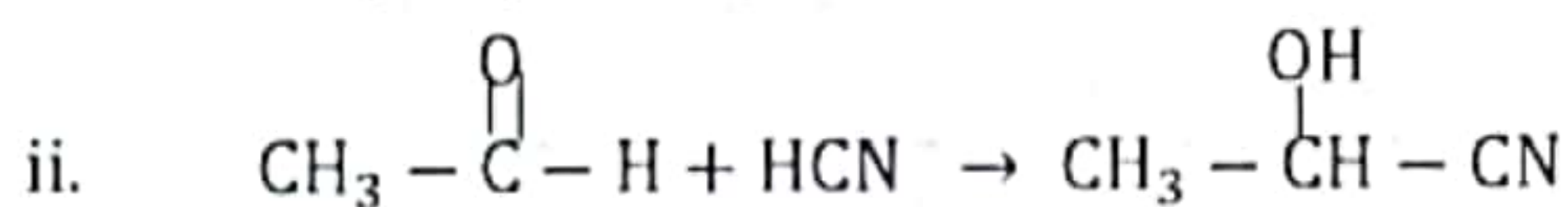
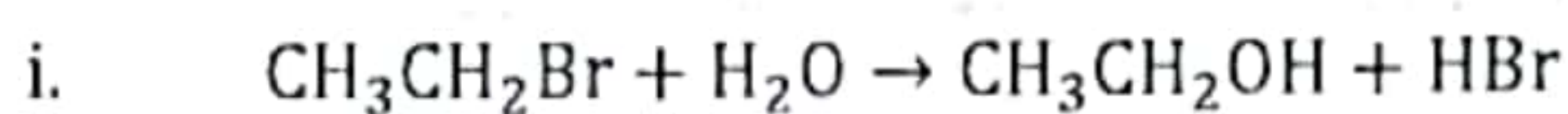
Problem 2

Explain how the following condition favor homolytic bond fission:

- Ultra violet light
- Very high temperature
- High voltage

Problem 3

Show reaction mechanism of the following organic reactions:



Chapter 4 FUNCTIONAL GROUPS

INTRODUCTION

Functional groups are group of atoms or bonds which determine characteristic chemical reactions of organic compound.

- It is the active site of organic compounds where chemical reaction takes place.

These groups of atoms or bonds determine how the compound **functions** chemically or reacts and hence the term functional groups.

- In the table below, there are some examples of common functional groups.

CLASS	FUNCTIONAL GROUP
Alkane	$\begin{array}{c} \quad \\ -C - C- \\ \quad \end{array}$
Alkene	$\begin{array}{c} \diagup \quad \diagdown \\ C = C \\ \diagdown \quad \diagup \end{array}$
Alkyne	$-C \equiv C-$
Aromatic compound	
Ether	$\begin{array}{c} \quad \\ -C - O - C- \\ \quad \end{array}$
Amine	$R - N \begin{array}{l} \diagup \\ \diagdown \end{array}$
Carbonyl compounds	$-CO-$ (Carbonyl group) i) $-CHO-$ (Aldehyde) ii) $RCOR$ (Ketone)
Carboxylic acids	$-COOH$ (Carboxylic group)
Amides	$-CON \begin{array}{l} \diagup \\ \diagdown \end{array}$
Esters	$-COOR$
Acid halide (acyl halide)	$-COX$ (acyl group); where X is halogen, e.g. $-COCl$ for acyl chloride.

HOMOLOGOUS SERIES

Organic compounds that have the same functional group have similar properties.

- These compounds are said to belong into the same **homologous series**.

Homologous series is a family of organic compounds containing a particular characteristic group and exhibiting similar properties.

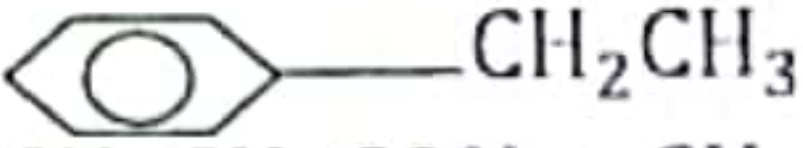
- Characteristics of homologous series are:
 - They have the same general molecular formula
 - Successive member differ by fixed unit of $-CH_2$
 - They have the same method of preparation
 - They have the same chemical properties (The same functional group)
 - They show gradual change in their physical properties e.g. boiling point of alkanes increase with an increase of number of carbons.
 - Their name end with the same suffix, e.g. names of all alkanes end with suffix $-ane$.

PRACTICE EXERCISE 4**Problem 1**

- a. Define the following terms:
- Functional group
 - Homologous series
- b. List down characteristics of homologous series

Problem 2

To what family does each of the following organic belongs?

- $\text{CH}_3\text{CH}_2\text{NHCH}_3$
- $\text{CH}_3\text{OCOCH}_3$
- 
- $\text{CH}_3\text{CH}_2\text{CON}(\text{CH}_3)_2$
- CH_3CHO
- $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$
- CHCH
- CH_3CHCH_2
- CH_3OCH_3
- CH_3COCH_3

Chapter 5

TYPES OF ORGANIC REACTIONS

Organic reactions can be grouped into four basic types which are:

- i) Substitution reactions
- ii) Addition reactions
- iii) Elimination reactions
- iv) Rearrangement/isomerisation reactions

Other types (some of them fall into the above mentioned categories) which will be discussed in the next chapters include:

- Combustion
- Condensation
- Polymerisation
- Hydrolysis
- Fermentation

SUBSTITUTION REACTIONS

Substitution reaction is the chemical reaction whereby atom or group of atoms is replaced by atom or group of atoms from the compound.

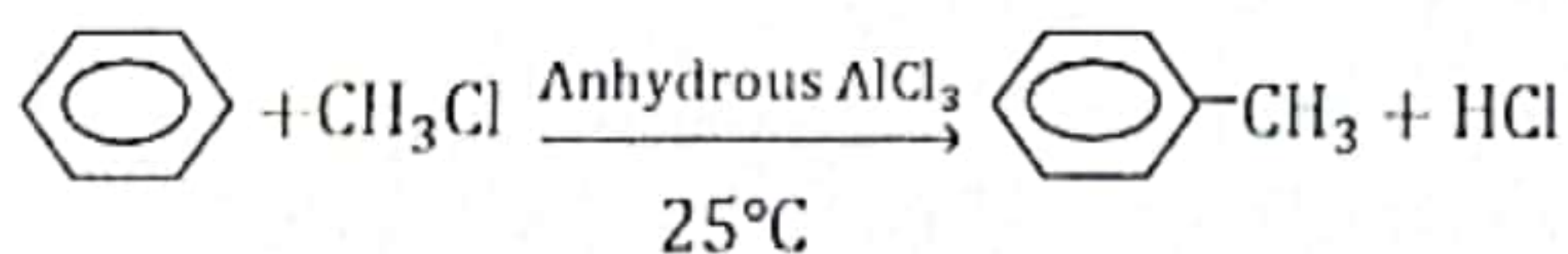
- According to type of reactant which is substituted to the molecule, substitution reactions can further be divided into three types, namely:

- a) Electrophilic substitution reactions (S_E)
- b) Nucleophilic substitution reactions (S_N)
- c) Free radical substitution reactions (S_R)

a) Electrophilic substitution reaction(S_E)

This is an organic reaction whereby atom or group of atoms is replaced by electrophile from the organic compound.

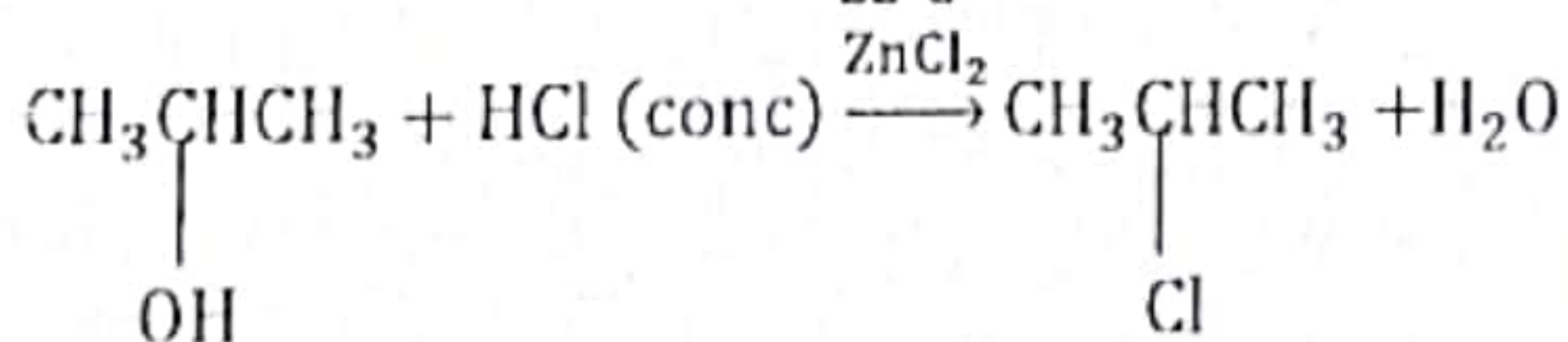
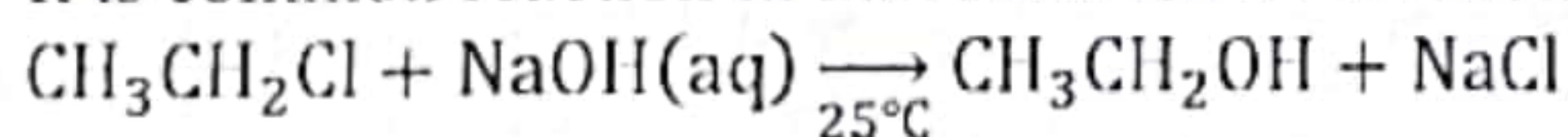
- It is common reaction in aromatic compounds. For example;



b) Nucleophilic substitution reaction(S_N)

This is an organic reaction where by atom (or group of atoms) is replaced by nucleophile from the organic compound.

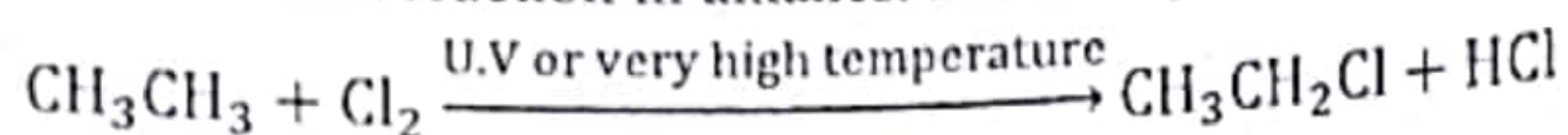
- It is common reaction in haloalkanes and alcohols. For examples;



c) Free radical substitution reaction (S_R)

This is an organic reaction whereby atom (or group of atoms) is replaced by free radical from organic compound.

- It is common reaction in alkanes. For example;

**ADDITION REACTIONS**

Addition reaction is the organic reaction whereby atoms (or groups of atoms) add to carbon atoms of unsaturated organic compound (or small sized ring of alkanes) resulting to formation of one product only.

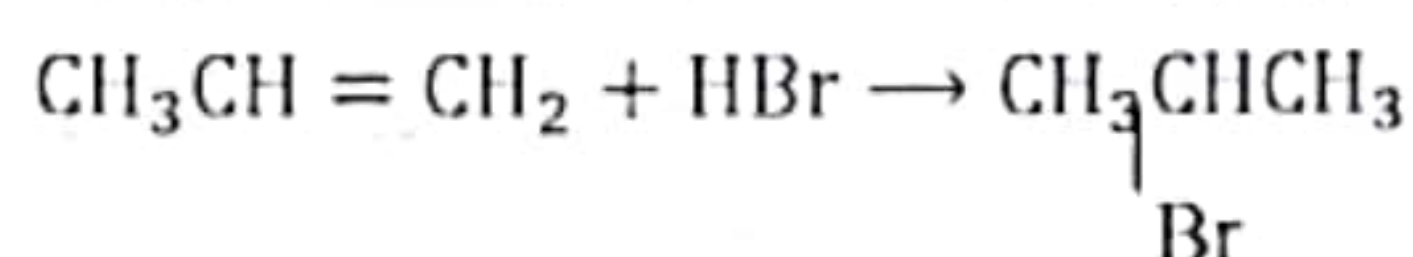
- It can further be divided into three types;

- Electrophilic addition reactions (A_E)
- Nucleophilic addition reactions (A_N)
- Free radical addition reactions (A_R)

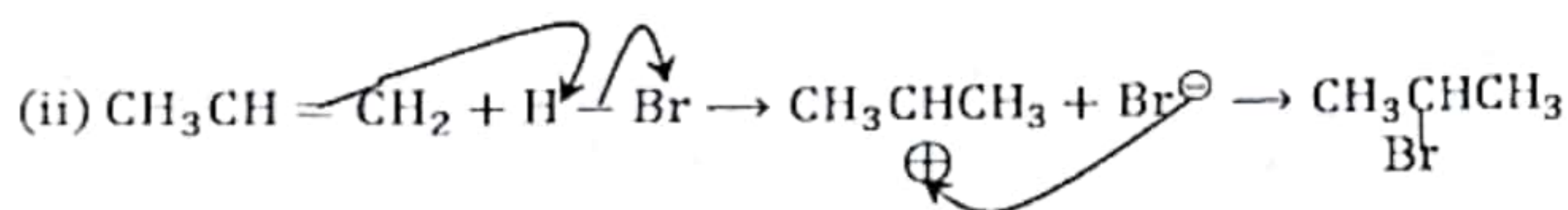
a) Electrophilic addition reactions (A_E)

This is the addition reaction whereby an electrophile is added first to carbon atom followed by a nucleophile.

- It is common reaction in alkenes and alkynes. For example;



To understand how electrophile is added first in the above reaction, study the mechanism of the reaction shown below.

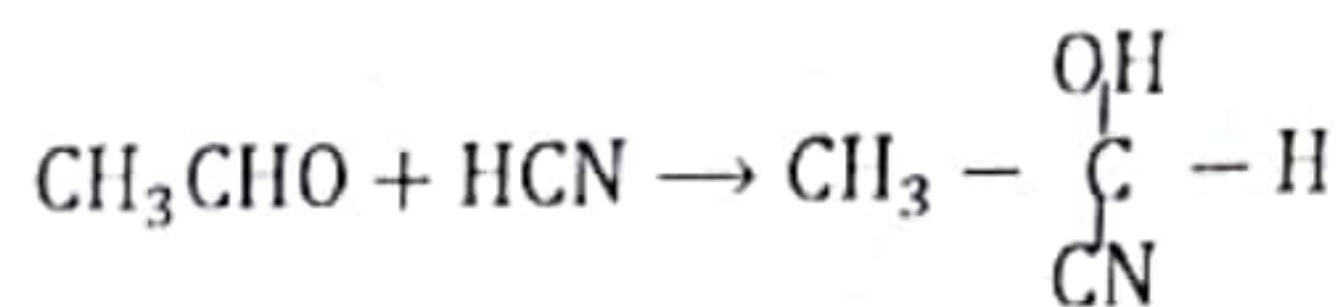


From the above mechanism it is clearly understood that H^+ (electrophile) is added first in the first step followed by Br^- (nucleophile) in the second step of the reaction mechanism.

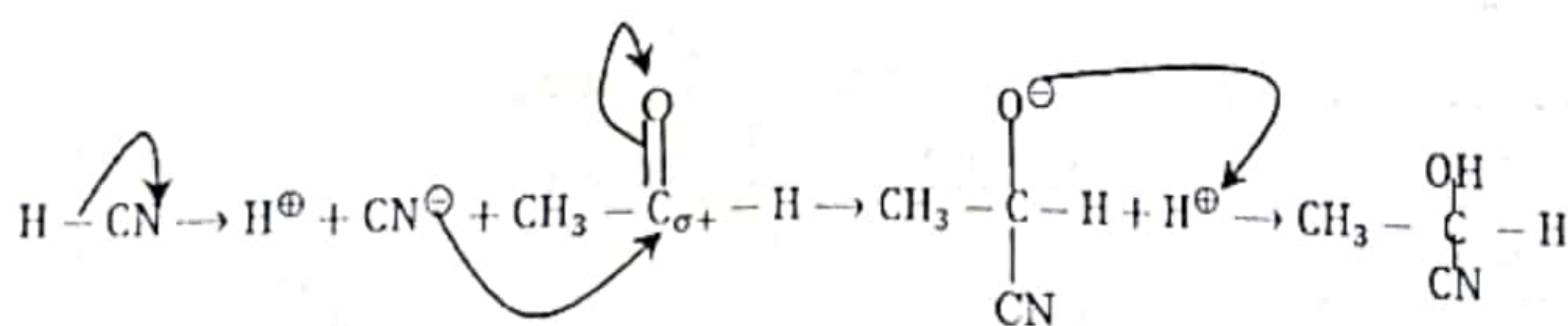
b) Nucleophilic addition reaction (A_N)

This is the addition reaction whereby nucleophile is added first to carbon atom followed by an electrophile.

- It is a common reaction in carbonyl compounds (aldehydes and ketones). For example;



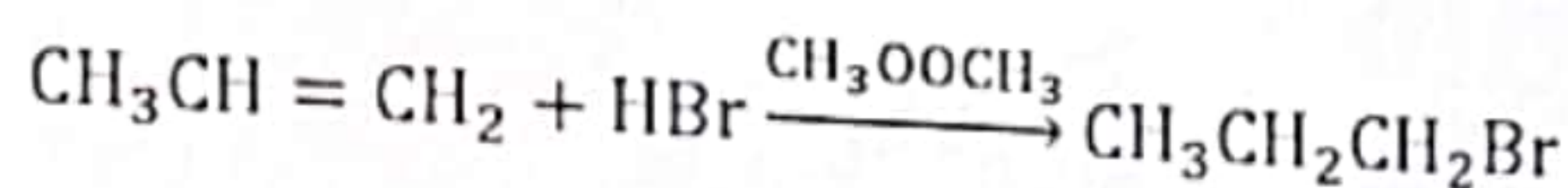
Again study mechanism below to understand how a nucleophile (CN^-) is added first in the above reaction.



Free radical addition reaction (A_R)

This is addition reaction which is brought about by free radicals i.e. free radicals are added to carbon atoms.

- A good example of this is the addition of hydrogen bromide to alkene under presence of organic peroxide (remember organic peroxide favours homolytic bond cleavage hence formation of free radicals).

**ELIMINATION RECTIONS**

This is an organic reaction whereby atoms (or groups of atoms) are removed from organic compound.

- If atoms are removed from adjacent carbon atoms it results to formation of multiple bonds (double or triple bonds) between those carbons, but if are removed from the same carbon, in most cases it leads to formation of cyclic organic compounds.

Elimination reactions can take place under acidic or basic medium.

- If elimination reaction takes place under acidic medium then the reaction is known as **acid induced elimination reaction**.
- If elimination reaction takes place under basic medium then the reaction is known as **base induced elimination reaction**.

So according to the medium in which elimination reaction takes place, elimination reactions can be divided into two types which are:

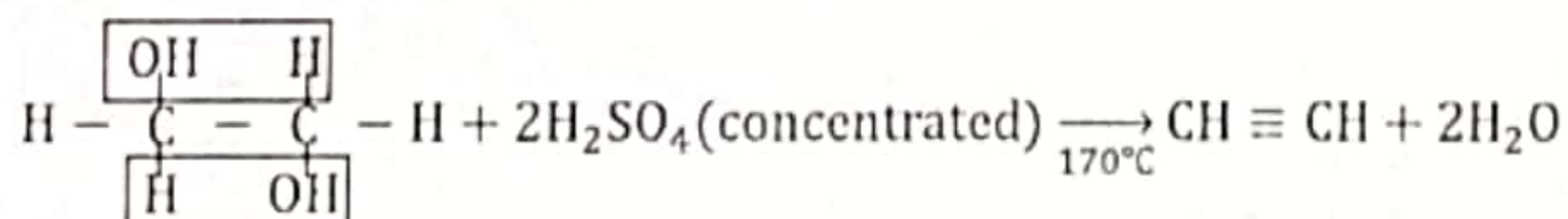
- **Acid induced elimination reaction and**
- **Base induced elimination reaction.**

Also elimination reactions can be classified into two types according to what carbons from which atoms are removed, namely:

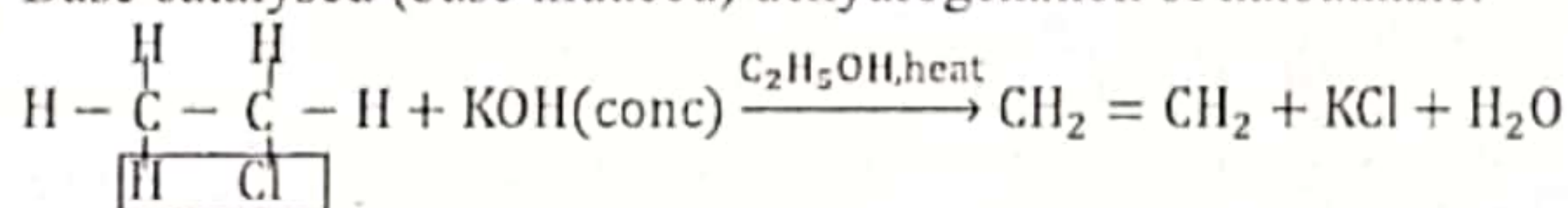
- **β -elimination reaction and**
- **α -elimination reaction**

β -elimination reaction is the elimination reaction whereby atoms or groups of atoms are removed from adjacent carbon atoms resulting to formation of multiple bonds (double or triple bond) between the two (adjacent carbon atoms). For example:

- Acid catalysed (acid induced) dehydrations of alcohols

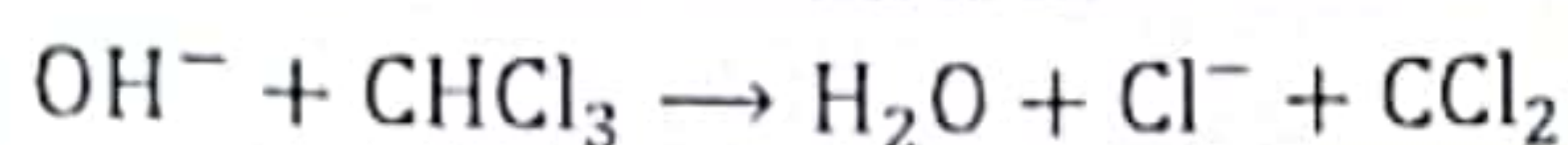


- Base catalysed (base induced) dehydrogenation of haloalkane.



α -elimination reaction is the elimination reaction in which all atoms are removed from a single carbon.

- A good example of this is hydrolysis of chloroform (trichloromethane) by base to form dichlorocarbene which is intermediate in carbylamine reaction and Reimer Tiemann reaction.



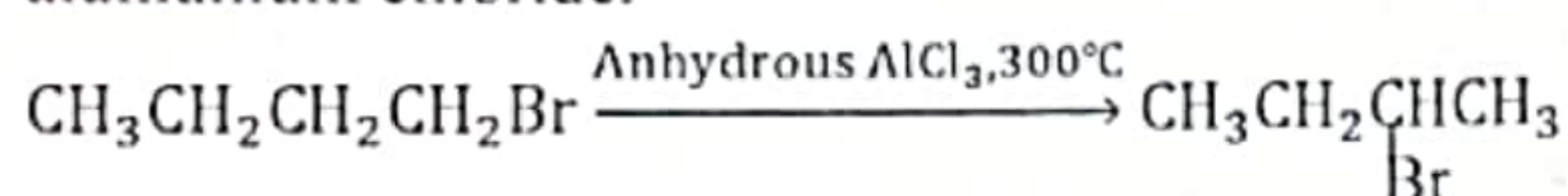
dichlorocarbene

Carbene is a neutral molecule of carbon which consists of two sigma bonds and one lone pair (Cl – $\ddot{\text{C}}$ – Cl). It is unstable intermediate.

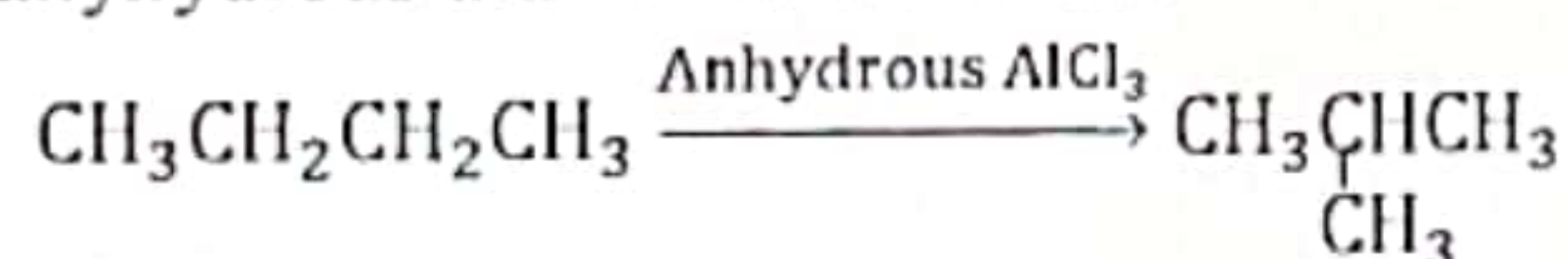
REARRANGEMENT REACTIONS

Rearrangement reaction is the organic reaction whereby atoms or group of atoms rearrange themselves in the molecule under influence of reagent or condition resulting to formation of new compound with the same atomic composition as the original one.

- The new compound formed in the rearrangement reaction has the same molecular formula as that of the original compound. In other words the compound formed is the isomer of the original compound hence the term **isomerisation reaction** for the rearrangement reaction. For example;
 - Rearrangement of bromobutane to form 2-bromobutane under influence of anhydrous aluminium chloride.

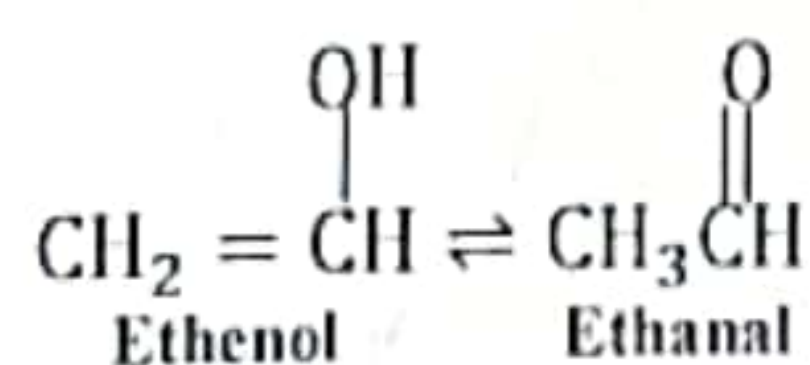


- Another example is rearrangement of n-butane to form 2-methylpropane under influence of anhydrous aluminium chloride.



When the rearrangement reaction give an isomer with different functional group to the original compound, the reaction is then known as **tautomerisation reaction** and the two isomeric compounds are known as **tautomers**.

- Tautomers are always in equilibrium to each other. For example, ethenol (unsaturated alcohol with C = C) can tautomerise into ethanal (aldehyde) where the hydrogen from OH group of the alcohol shift to carbon chain while the double bond of C = C shifts to C = O of carbonyl group of the aldehyde.



It should be understood that:

- Most of tautomerisation takes place in this way, i.e. it involves shifting of position of hydrogen accompanied with necessary shift of the double bond.
- The two tautomeric forms differ in their stability. The less stable form is called the **labile form**. For example in the above example ethenol is labile tautomer.

Definition of terms

Tautomerisation is the type of isomerisation reaction in which a compound exist in two readily interconvertible different structures leading to dynamic equilibrium.

Tautomers are isomers of organic compounds that readily interconvert by a chemical reaction called **tautomerisation**.

PRACTICE EXERCISE 5

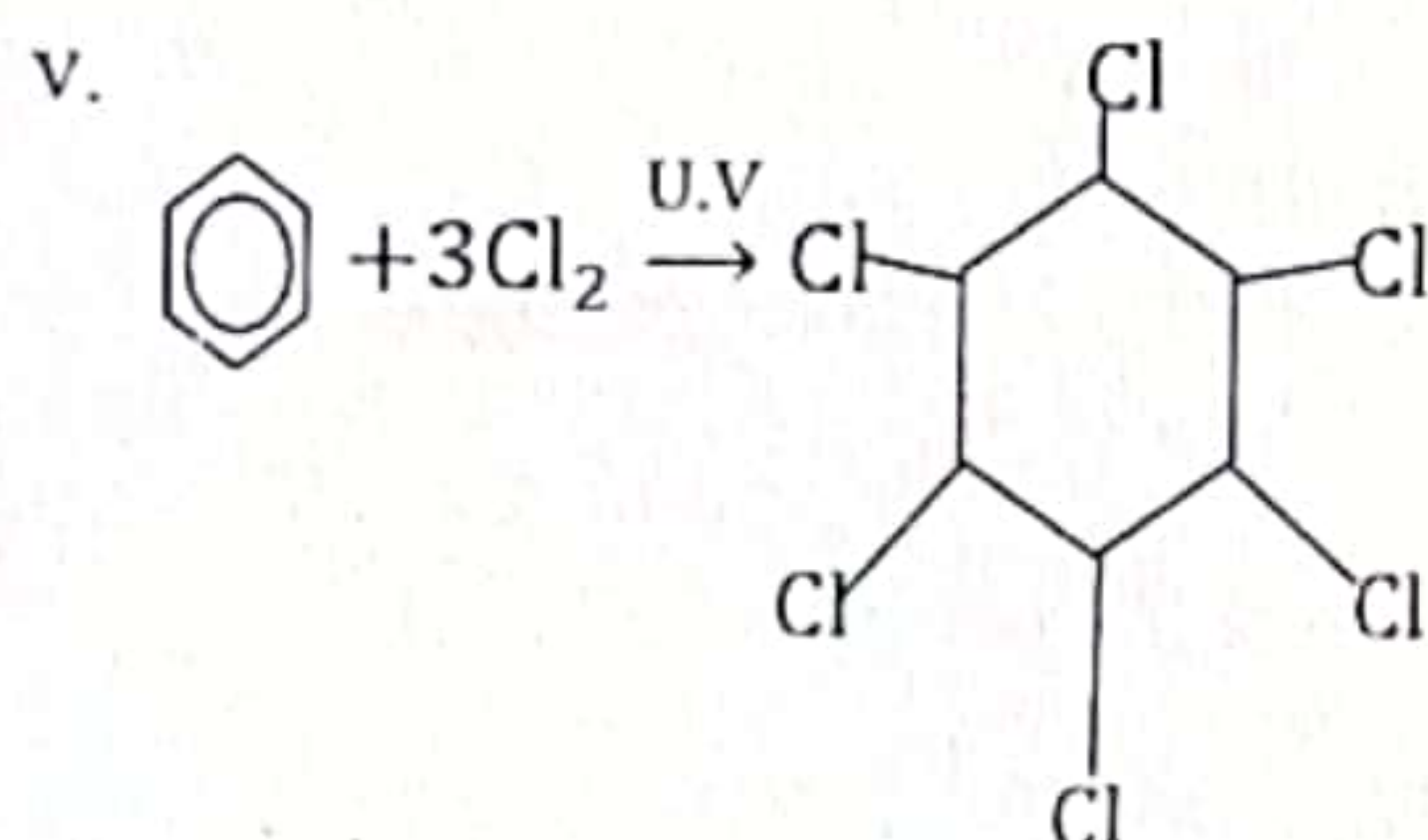
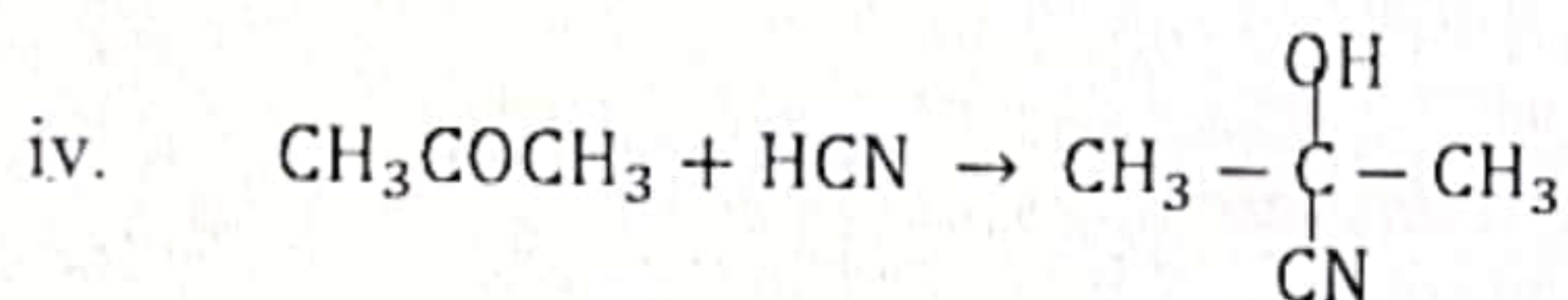
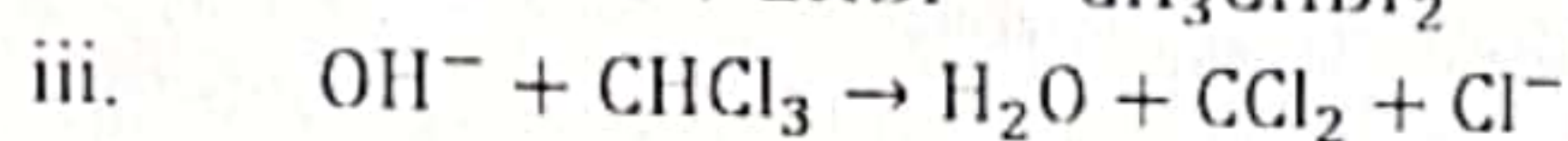
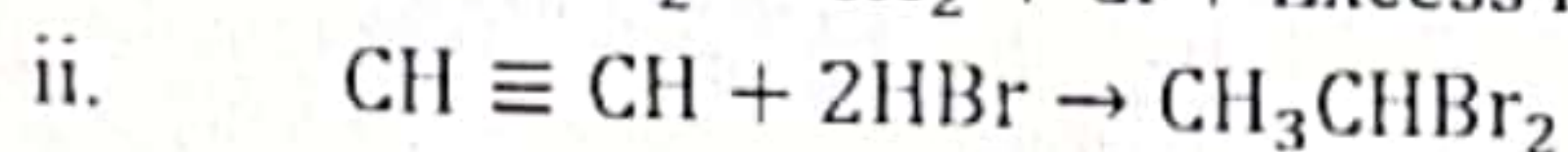
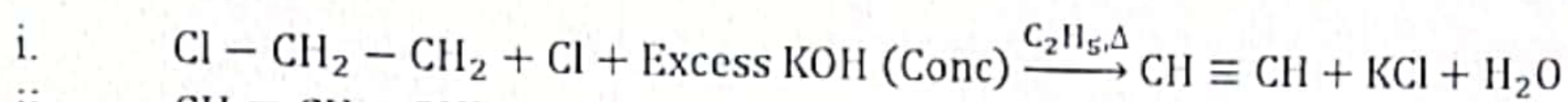
Problem 1

Define the following terms (give one example for each).

- i. Free radical substitution reaction
- ii. Free radical addition reaction
- iii. Nucleophilic substitution reaction
- iv. Electrophilic addition reaction
- v. Nucleophilic addition reaction
- vi. Base induced β -elimination reaction
- vii. Rearrangement reaction
- viii. Tautomerisation reaction
- ix. Acid induced β -elimination reaction

Problem 2

Give a type for each of the following organic reactions:



Is the product in (v) above aromatic or aliphatic in nature?

Chapter 6

FACTORS AFFECTING MECHANISM OF ORGANIC REACTIONS

Chemical reactions follow certain pathway before forming product (s). This pathway is known as reaction mechanism studied in the **chapter 3**.

- Any factor which affect this pathway called reaction mechanism, automatically affect the overall reaction and therefore factors affecting mechanism of organic reaction may also termed as factors affecting organic reactions.

Overall reaction and final product of any organic reaction depends much on nature and behaviour of initial reactant (s) in the reaction and that of intermediate product (s) in the elementary reaction.

- So before studying in detail factors affecting mechanism of organic reaction it is important to have better understanding in organic intermediates first.

ORGANIC REACTION INTERMEDIATES

Three important organic intermediates to study in this book are:

- Carbanion
- Carbocation
- Free radical

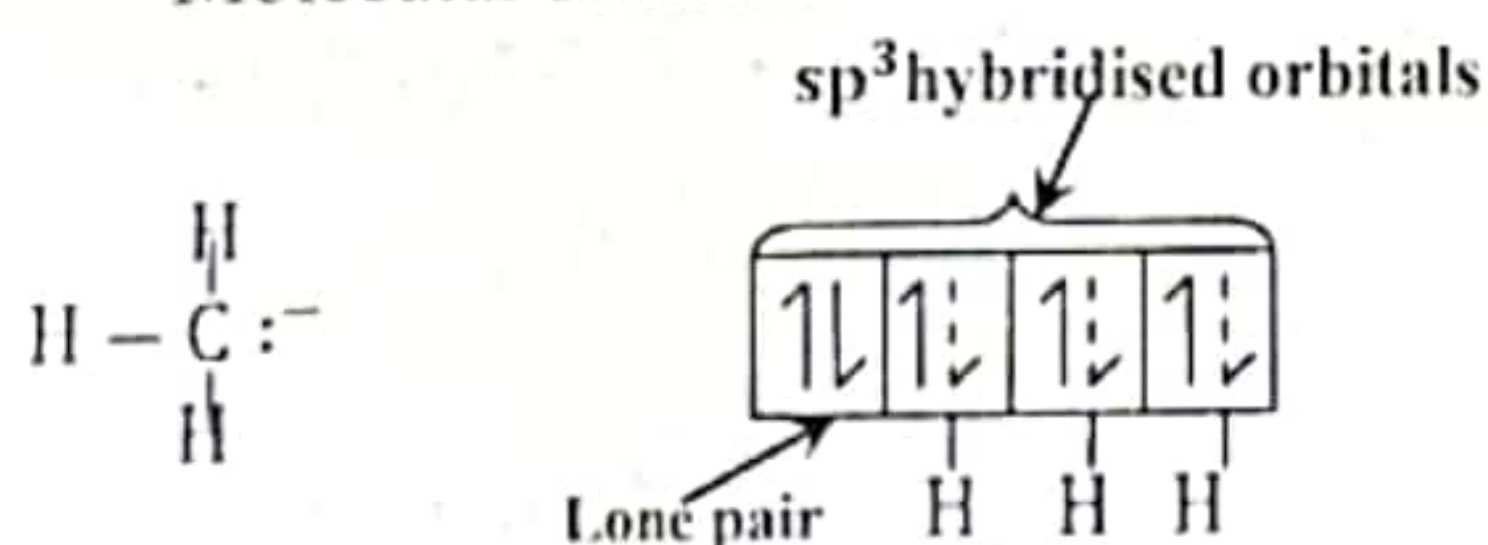
Carbanion.

Carbanion is the organic molecule with negatively charged carbon.

- It is commonly formed by heterolytic bond cleavage of the bond between carbon and stronger electropositive element. Since it is rare for carbon to form bond directly with strong electropositive element (metal), carbanions are not common.
- The carbon with negative charge has three bonds and one lone pair in the negative charge.

The simplest carbanion is methyl carbanion which has three sigma bonds in sp^3 hybridised orbitals and one lone pair resembling to ammonia. So methyl carbanion and ammonia are **isoelectronic**.

- Molecular structure and electronic structure of methyl carbanion are shown below:



So now it is clearly understood that methyl carbanion has the same electronic structure as that of ammonia, i.e. they are isoelectronic. Both having lone pair, the intermediate methyl carbanion and ammonia are nucleophiles. Now the question becomes, *of the two which one is stronger nucleophile?*

- Methyl carbanion being negative charged is stronger nucleophile than uncharged ammonia.

Presence of negative charge explains why carbanions are unstable organic intermediates.

Carbocation

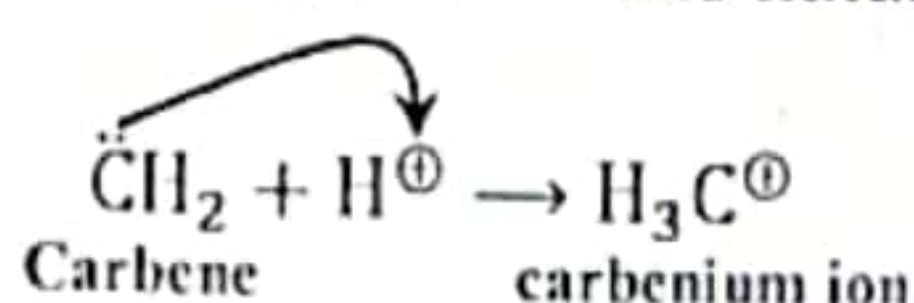
Carbocation is the organic molecule with positively charged carbon.

- It may be **carbenium ion** or **carbonium ion**.

Carbenium ion

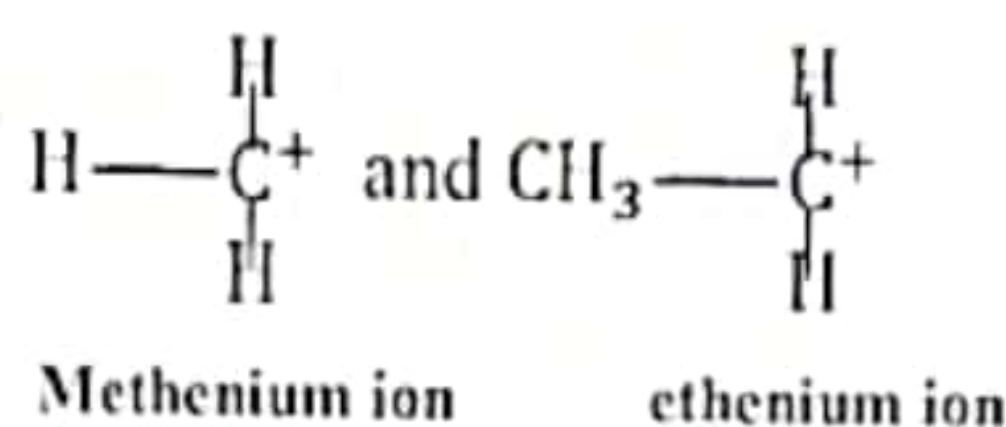
This is the organic molecule with positively charged carbon in trivalent state.

- It is commonly formed by heterolytic bond cleavage between carbon and stronger electronegative element. Since bonds between carbon and strong electronegative element like halogens are very common, carbenium ions are more common than carbanions.
- Positively charged carbon in carbenium ion has three bonds in sp^2 hybridised orbitals and single empty orbital. This resembles to situation when carbene (CH_2) has received hydrogen proton hence the name carbenium ion for all carbocations of this nature.



- Having incomplete octet structure accompanied with positive charge, carbenium are highly unstable organic intermediate.

Examples of carbenium ions are:



Among the two types of carbocations in this book will be more concerned with this type of carbocation (carbenium ion).

Carbonium ion

This is the organic molecule with positively charged carbon in the pentavalent state.

- It is formed when hydrocarbon reacts with very strong concentrated acid such that it becomes possible for the hydrocarbon to accept hydrogen proton from the acid.
- For example corresponding carbonium ion from CH_4 (methane) is **methanium ion**, CH_5^+ , (Relate it with ammonium ion, NH_4^+ , which is formed when ammonia, NH_3 , accept hydrogen proton). Another example of carbonium ion is **ethanium ion**, C_2H_7^+ , ($\text{CH}_3 - \text{CH}_4^+$). Also **ethynium ion**, C_2H_3^+ ($\text{CH} \equiv \text{CH}_2^+$).

Since the reaction which leads to formation of carbonium ion is not common, carbonium ions are not common too.

Don't be confused!

In previous years the term carbonium ion was used to represent all carbocations including carbenium ions. However nowadays technically the term is no longer in use although some people continue to misuse the term 'carbonium ion' in place of 'carbenium ion'.

Free radicals

As far as organic chemistry is concerned, **free radical** is the organic molecule with single unpaired electron.

- It is formed by homolytic bond cleavage between carbon and atom of another element.
- Due to presence of unpaired electron, free radicals are highly reactive organic intermediate.

Carbon with unpaired electron in free radical has three bonds in sp^2 hybridised orbital and one orbital with unpaired electron (Compare it with carbenium ion where there are three sp^2 hybridised orbitals and one empty orbital in the positively charged carbon)

- Example of free radical is methyl radical, $\text{H}_3\text{C}^\bullet$

FACTORS AFFECTING MECHANISM OF ORGANIC REACTION

There are various factors which determine nature and behaviour of reactants and intermediates of organic reactions.

- Important factors to study in this book are:
 - Inductive effect
 - Mesomeric effect and
 - Steric effect

Inductive and mesomeric effects altogether in combination are known as **electronic effect** because their effect is determined by movement of electrons.

INDUCTIVE EFFECT

Inductive effect arises in the organic compound as results of partial withdraw of electrons from the functional group (or group of carbon atoms) or partial supply of electrons towards the functional group (or group of carbon atoms).

- It can further be divided into two types;
 - Negative inductive effect ($-I$)
 - Positive inductive effect ($+I$)

Negative inductive effect ($-I$)

This is the effect which arises in organic compounds as results of partial withdraw of electrons from the functional group (or group of carbon atoms).

- Negative inductive effect is brought about by the strong electronegative radicals or atoms of element with high electronegativity; for example: F, Cl, and Br (halogens), O (oxygen atom), HO^- and RO^- where R is a group containing carbon atoms.

If the element is stronger electronegative then its atom is said to cause stronger negative inductive effect and vice-versa; e.g. F being stronger electronegative than Cl, exerts stronger negative inductive effect.

- Generally strength of negative inductive effect exerted by halogens follows the following trend:



$\xrightarrow{\hspace{1.5cm}}$
 Decrease in $-I$ exerted by halogens

How negative inductive effect affects mechanism of organic reaction?

Negative inductive effect affects mechanism of organic reactions in the following ways;

1. Increases stability of carbanion

Negative inductive effect increases stability of carbanion as a result of partial withdraw of electrons from the negatively charged carbon of the carbanion thus decreasing the negative charge intensity in the carbanion. In other words negative inductive effect leads to the partial neutralisation of the negative charge by making the carbanion less negative.

Three points to note!

- If a carbanion has stronger electronegative atom which cause stronger negative inductive effect then the carbanion will be more stable.
- If a carbanion has greater number of strong electronegative atoms then the carbanion will experience stronger negative inductive effect and hence it will be more stable.

- If a carbanion has strong electronegative atom closer to the negatively charged carbon then the carbon will experience stronger negative inductive effect and hence the carbanion will be more stable.

Example 1

Between $\text{CH}_2\text{FC} \equiv \text{C}^-$ and $\text{CH}_2\text{ClC} \equiv \text{C}^-$, which one is more stable. Explain.

Solution

The stability of given carbanions has been increased by negative inductive effect exerted by F and Cl which are strong electronegative element. F being stronger electronegative element exerts stronger negative inductive effect and hence $\text{CH}_2\text{FC} \equiv \text{C}^-$ is more stable.

Example 2

For each of given pair of carbanions given below, select the more stable carbanion.

- (a) $\text{CH}_2\text{FC} \equiv \text{C}^-$ and $\text{CHF}_2\text{C} \equiv \text{C}^-$ (b) $\text{CHCl}_2\text{CH}_2\text{C} \equiv \text{C}^-$ and $\text{CH}_3\text{CHClC} \equiv \text{C}^-$
 (c) $\text{CHCl}_2\text{CH}_2\text{C} \equiv \text{C}^-$ and $\text{CH}_2\text{ClCHClC} \equiv \text{C}^-$

Solution

- (a) $\text{CHF}_2\text{C} \equiv \text{C}^-$ (b) $\text{CHCl}_2\text{CH}_2\text{C} \equiv \text{C}^-$ (compound with greater number of strong electronegative atoms experience stronger negative inductive effect regardless to their position) (c) $\text{CH}_2\text{ClCHClC} \equiv \text{C}^-$

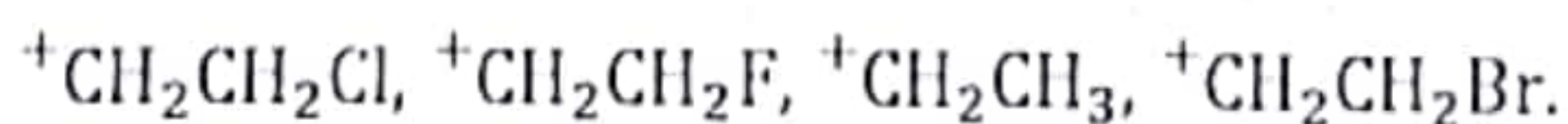
2. Decreases stability of carbenium ion

Negative inductive effect decreases stability of carbenium ion by making the ion more positive as result of partial withdraw of electrons.

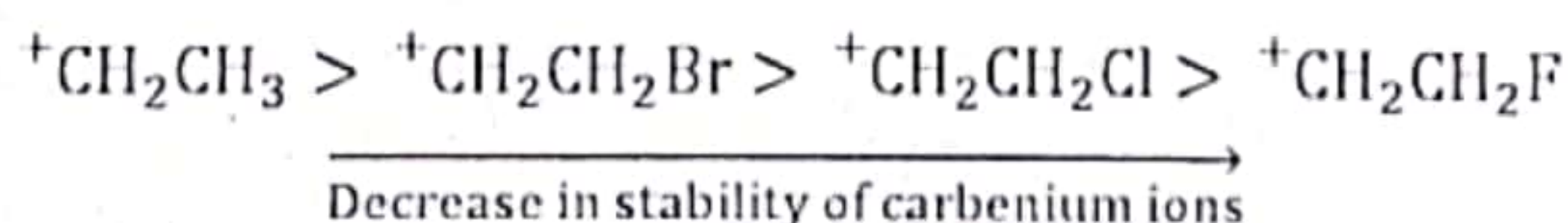
- If the carbenium ion has stronger electronegative atom which cause stronger negative inductive effect then the ion will be less stable.
- If a carbenium ion has greater number of strong electronegative atoms then the carbenium ion will experience stronger negative inductive effect and hence it will be less stable.
- If a carbenium ion has strong electronegative atom closer to the positively charged carbon then the carbon will experience stronger negative inductive effect and hence the carbenium ion will be less stable.

Example 3

Arrange the following ions in decreasing order of their stability



Solution

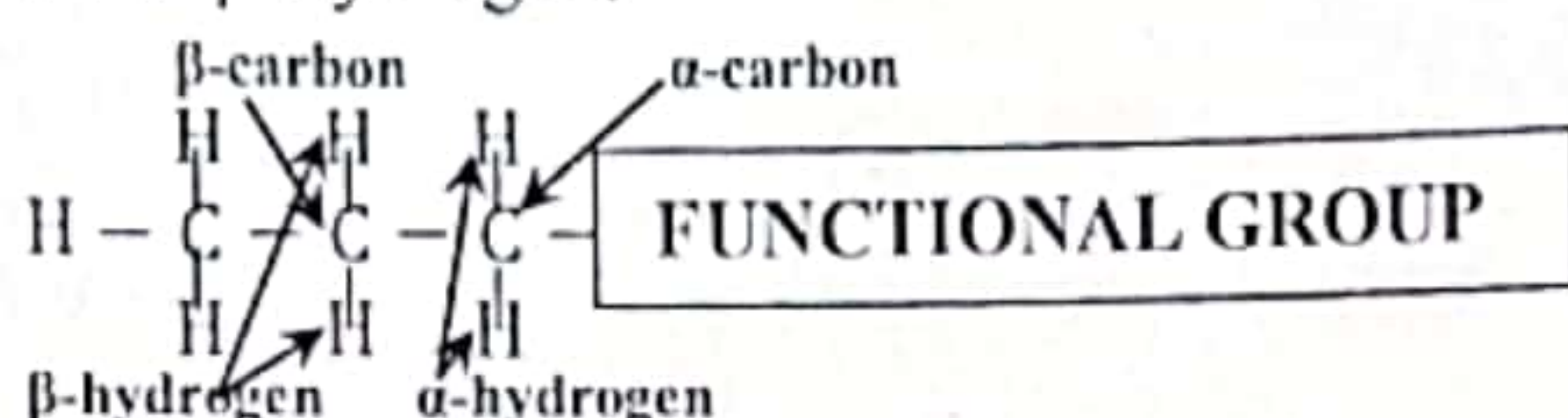


3. Accounts for acidic behaviour of α and β hydrogens in haloalkanes

Haloalkane is an organic compound which is formed when at least one hydrogen atom of alkane is replaced by halogen; e.g. $\text{CH}_3\text{CH}_2\text{Cl}$.

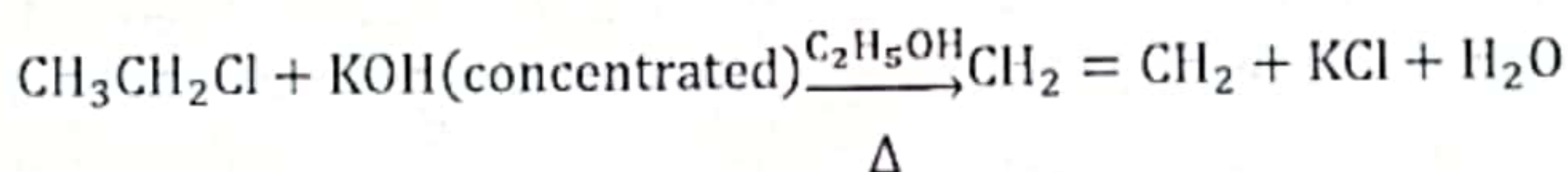
- A carbon which is directly bonded to functional group is known as α -carbon and hydrogen bonded to it are known as α -hydrogen.

- A carbon which is directly bonded to α -carbon is known as β -carbon and hydrogen bonded to it is known as β -hydrogen.



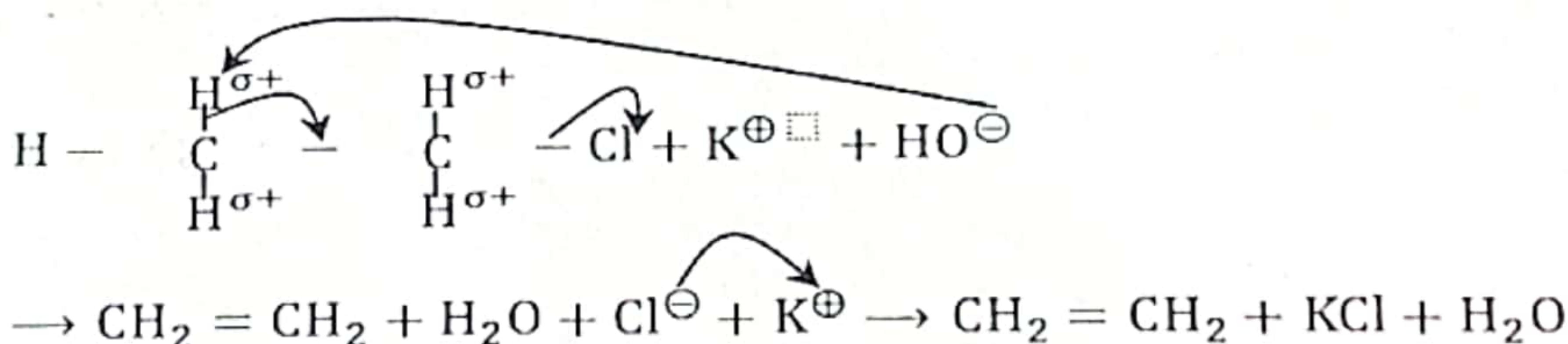
Usually organic reactions occur at an active site which is known as functional group but this is any time when the organic compound is not bonded to strong electronegative atoms like halogens.

- In presence of strong electronegative atom like halogens in haloalkane, there is partial withdraw of electrons from C – X bond in neighbour carbon atoms (α -carbon and β -carbon) thus making hydrogens bonded to those carbon atoms more positive polarised and hence they become acidic. The situation is not experienced by hydrogens in carbons which are far from functional group (it experienced by α and β hydrogens only which are closer to the nucleus).
- Under presence of strong concentrated alkaline solution, these acidic α and β hydrogens have high affinity to base thus making possible for chemical reaction to take place in α and β carbons apart from functional group.
- A clear example of this is when haloalkane like chloroethane is reacted with concentrated alkaline solution like KOH under presence of heat and alcohol.

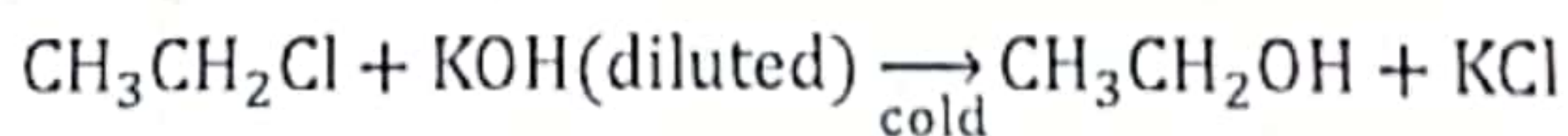


To have better understanding how the reaction occurs, study its mechanism shown below.

Mechanism



But when the alkaline solution and temperature lowered to 0°C , the reaction takes place at functional group only and alcohol as expected.



(On your own write the reaction mechanism to study how in this case the reaction takes place at functional group only).

NEGATIVE INDUCTIVE EFFECT AND INCREASE IN ACIDIC STRENGTH OF CARBOXYLIC ACIDS

Acidic strength of a compound is determined by its ability of releasing hydrogen proton (H^+).

- If the compound has high ability of releasing proton then the compound has high acidic strength and vice versa.

So any factor which affects ability of releasing hydrogen proton in the compound is said to affect the acidic strength of the compound.

In the case of carboxylic acids (its functional group $-COOH$), the acidic strength is determined by ability of its $O-H$ to undergo heterolytic cleavage so as to release hydrogen proton and stability of carboxylate ion which is formed after releasing of hydrogen proton by the acid.

On another hand the cleavage of $O-H$ bond depends on the strength of $O-H$ bond i.e. if the bond is weak then the $O-H$ bond breaks easily to give hydrogen proton and vice-versa..

Presence of strong electronegative atoms like halogens in carboxylic acid, leads to partial withdraw of electrons from functional group (carboxylic group) including electrons in $O-H$ bond thus decreasing the electron density in the bond. This makes $O-H$ bond weaker and hence it becomes easier to release H^+ and for that reason acidic strength is increased.

Also carboxylate ion formed after releasing H^+ is stabilised by partial withdraw of negatively charged electrons brought about by strong electronegative atom present.

- This increases the ability of carboxylate ion to exist on its own without combining with released H^+ . This is another way of which acidic strength of carboxylic acid is increased by presence of strong electronegative atom.

Are these electronegative atoms which cause what we call negative inductive effect hence negative inductive effect increases acidic strength of carboxylic acids.

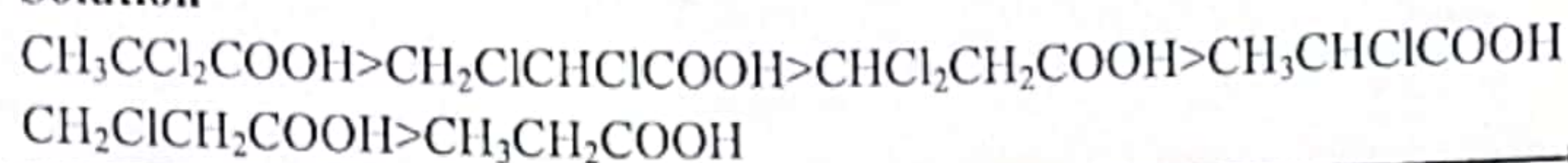
- So in conclusion we may say that negative inductive effect increases acidic strength of carboxylic acid by;
 - Making easier to release H^+
 - Stabilizing carboxylate ion

Important concepts about $-I$ in relation to acidic strength of carboxylic acids

- If two carboxylic acids with same number of carbon are bonded to two different strong electronegative atoms (one atom in each acid) then the acid which contains stronger electronegative atom will be stronger acid. For example, CH_2FCOOH is stronger acid than $CH_2ClCOOH$ because F being more electronegative than Cl causes stronger $-I$.
- If two carboxylic acids with the same number of carbon atoms of the same element which cause $-I$ then the acid with greater number of atoms which cause $-I$ will be stronger acid. For example, $CHCl_2COOH$ is stronger acid than $CH_2ClCOOH$.
- If two carboxylic acids with the same number of carbons are bonded to the same number of the same atom (s) which cause $-I$, but atoms in the two acids are bonded in different way then the acid with atom(s) closer to the functional group (i.e. of carboxylic group) will be stronger acid.

Example 4

Arrange the following cpds according to decrease in acidic strength $\text{CH}_2\text{ClCHClCOOH}$, $\text{CH}_2\text{ClCH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CHCl}_2\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CHClCOOH}$, $\text{CH}_3\text{CCl}_2\text{COOH}$.

Solution

Decrease in acidic strength $\longrightarrow$

Example 5

CH_2ClCOOH is stronger acid than CH_2BrCOOH . Explain.

Solution

In given acids, acidic strength has been increased by $-I$ brought about by halogens (Cl and Br) which are strong electronegative elements; Cl being more electronegative it cause stronger $-I$ than Br and hence CH_2ClCOOH will be stronger acid.

NEGATIVE INDUCTIVE EFFECT AND DEREASE IN BASIC STRENGTH OF AMINES

Amine is an organic compound which is formed when at least one hydrogen atom of ammonia is replaced by alkyl or aryl group, e.g RNH_2 where R is alkyl group.

- Basic character of amine is explained by presence of one lone pair in nitrogen thus acting as lewis base by donating its lone pair electrons to lewis acid.

Basic strength of amine is determined by participation of its lone pair in chemical reaction.

- If lone pair electrons are more available in participating in chemical reaction then the amine will be stronger base and vice-versa.

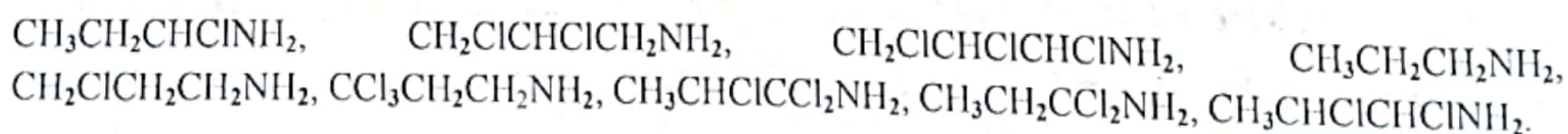
So any factor which affects participation of lone pair electrons of amine in chemical reaction is said to effect basic strength of the amine.

- Presence of strong electronegative atom (like halogens) in amine leads to partial withdraw of lone pair electrons in amine, thus making more difficult for lone pair electrons to participate in organic reaction and hence basic strength is decreased.
- Also these strong electronegative atoms decrease basic strength of amine by destabilizing a positive charge formed on nitrogen after accepting hydrogen proton (H^+) making the charge more positive through partial withdraw of electrons from the positively charged nitrogen.

Are these strong electronegative atoms which causes negative inductive effect ($-I$) and hence negative inductive effect decreases basic strength of amine.

Example 6

Arrange the following organic compounds in order of increase in their basic strengths starting with the weakest base.



Solution

1. $\text{CH}_3\text{CHClCCl}_2\text{NH}_2$
2. $\text{CH}_2\text{ClCHClCHClNH}_2$
3. $\text{CCl}_3\text{CH}_2\text{CH}_2\text{NH}_2$
4. $\text{CH}_3\text{CH}_2\text{CCl}_2\text{NH}_2$
5. $\text{CH}_3\text{CHClCHClNH}_2$
6. $\text{CH}_2\text{ClCHClCH}_2\text{NH}_2$
7. $\text{CH}_3\text{CH}_2\text{CHClNH}_2$
8. $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{NH}_2$
9. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

Exmple 7

$\text{CH}_3\text{CHBrNH}_2$ is stronger base them $\text{CH}_3\text{CHClNH}_2$. Explain.

Solution

In given compounds, basic strength has been decreased by -I which is brought about by halogens (Cl and Br) which are strong electronegative elements. But Cl being stronger electronegative than Br, causes stronger -I than Br and hence $\text{CH}_3\text{CHBrNH}_2$ becomes stronger base.

Positive inductive effect (+I)

This is the effect which arises in organic compounds as a result of partial supply of electrons to the functional group or group of carbon atoms.

- Positive inductive effect is brought by presence of an electron releasing group mainly alkyl groups in organic compound.

-The amount of positive inductive effect exerted by an alkyl group depends on its length of carbon chain, i.e. the longer the carbon chain the stronger positive inductive effect is and vice versa. For example ethyl group (CH_3CH_2-) exerts stronger positive inductive effect than methyl group (CH_3-)

Why is alkyl an electron releasing group?

Carbon is slightly more electronegative than hydrogen. So in an alkyl group, for example, a methyl group (CH_3-), methyl carbon pulls bonded electrons from the three hydrogen atoms nearer to carbon, and eventually the carbon acquires a partial negative charge and correspondingly, hydrogen loses some attraction with bonded electrons and acquires a partial positive charge.

- Thus carbon gets a little more electronic charge which the carbon will push towards the group to which it is linked and hence the methyl group will be electron releasing in nature.
- In an ethyl group (CH_3CH_2-), this effect will be more than methyl. The CH_3 part of the ethyl group releases electrons to the next carbon plus two hydrogens (in CH_2 part) also make contributions and hence the net electron releasing effect of ethyl group is more than that of a methyl group.

In one sentence!

Carbon being more electronegative than hydrogen, alkyl carbon of an alkyl group pulls electron from hydrogen making it more negative and hence becomes electron donating to a group it bonded with.

How positive inductive effect affects mechanism of organic reaction?

Positive inductive effect affects mechanism of organic reaction in the following ways;

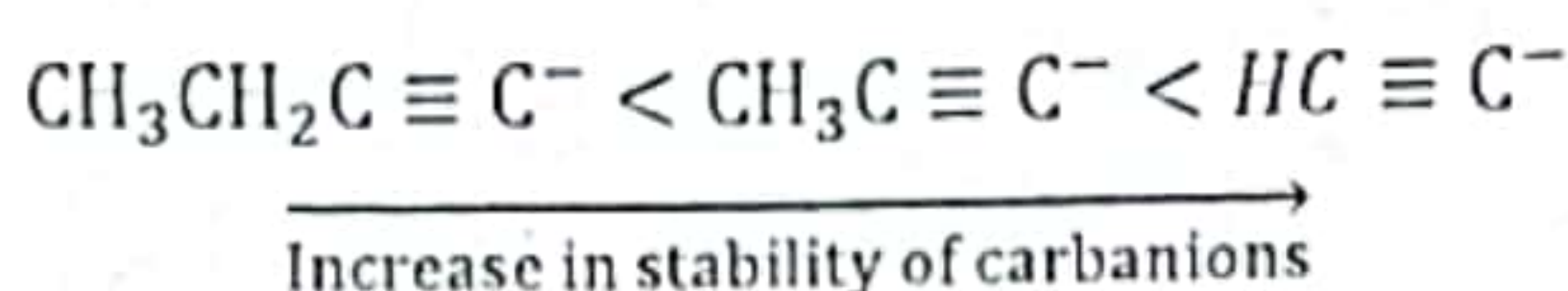
1. Decreases stability of carbanion

Positive inductive effect, decreases stability of carbanion by making the ion more negative as result of partial releasing of electrons towards the charged carbon.

- So the carbanion with longer chain is less stable than carbanion with shorter carbon chain due to an increase in positive inductive effect as length of carbon chain increases.

Example 8

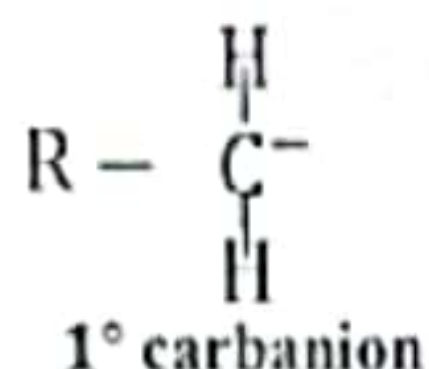
Arrange the following ions in order of increasing of their stability

**Solution**

Also on basis of number of alkyl groups bonded to the carbon with alkyl groups, carbanions can be classified into three categories, namely;

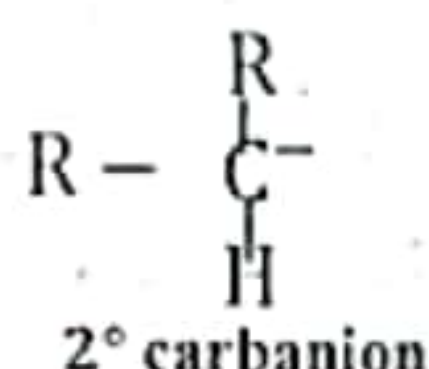
- Primary (1°) carbanion
- Secondary (2°) carbanion
- Tertiary (3°) carbanion

Primary (1°) carbanion is the one with only one alkyl group bonded to the negatively charged carbon.



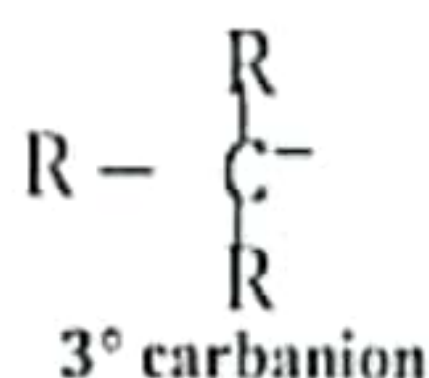
- 1° carbanion receives positive inductive effect from one alkyl group from one direction only.

Secondary (2°) carbanion is the one with two alkyl groups bonded to the negatively charged carbon.



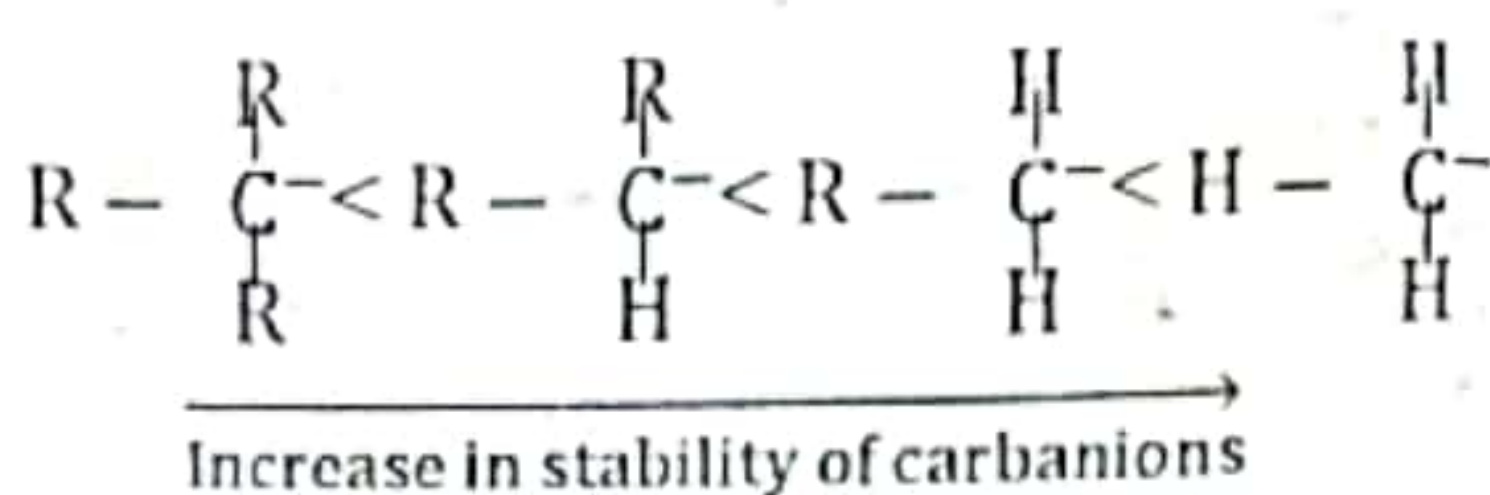
- So 2° carbanion receives positive inductive effect from two alkyl groups from two directions. It is stronger positive inductive effect than that received by 1° carbanion.

Tertiary (3°) carbanion is the one with three alkyl groups bonded to the negatively charged carbon.



So 3° carbanion receives positive inductive effect from three alkyl groups from three directions. It experience strongest positive inductive effect of all classes of carbanion.

Therefore stability of different classes of carbanions follows the following order:



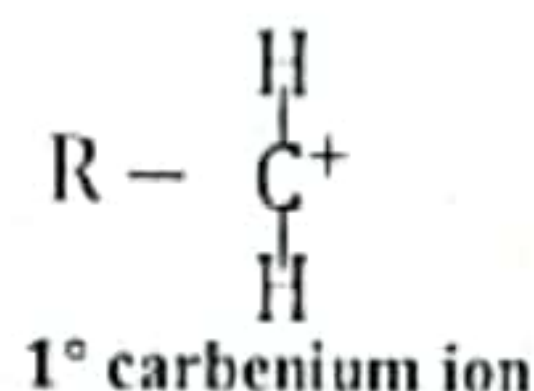
2. Increases stability of carbenium ion

Positive inductive effect stabilises carbenium ion by doing partial neutralisation of positively charged carbon as a result of partial supply of electrons to the carbon (positively charged carbon) thus making it less positive.

- So if the ion has longer carbon chain than the carbenium will be more stable and vice versa, e.g. $\text{CH}_3\text{CH}_2\text{C}^+ - \text{H}$ is more stable than $\text{CH}_3\text{C}^+ - \text{H}$ because CH_3CH_2 in the first ion exert stronger positive inductive effect than CH_3 in the second ion.

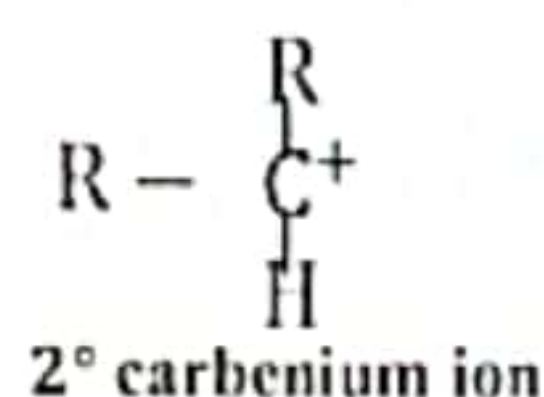
As in the case of carbanions, carbenium ions can be classified into three categories.

- (i) **Primary (1°) carbenium ion** is the one with only one alkyl group bonded to the positively charged carbon.



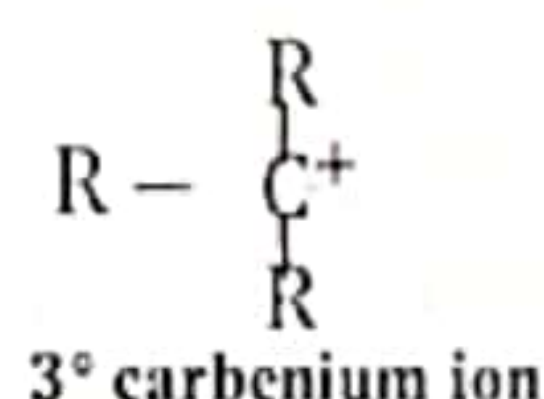
- 1° carbenium ion receives positive inductive effect from one alkyl group from one direction only.

- (ii) **Secondary (2°) carbenium ion** is the one with two alkyl groups bonded to the positively charged carbon.



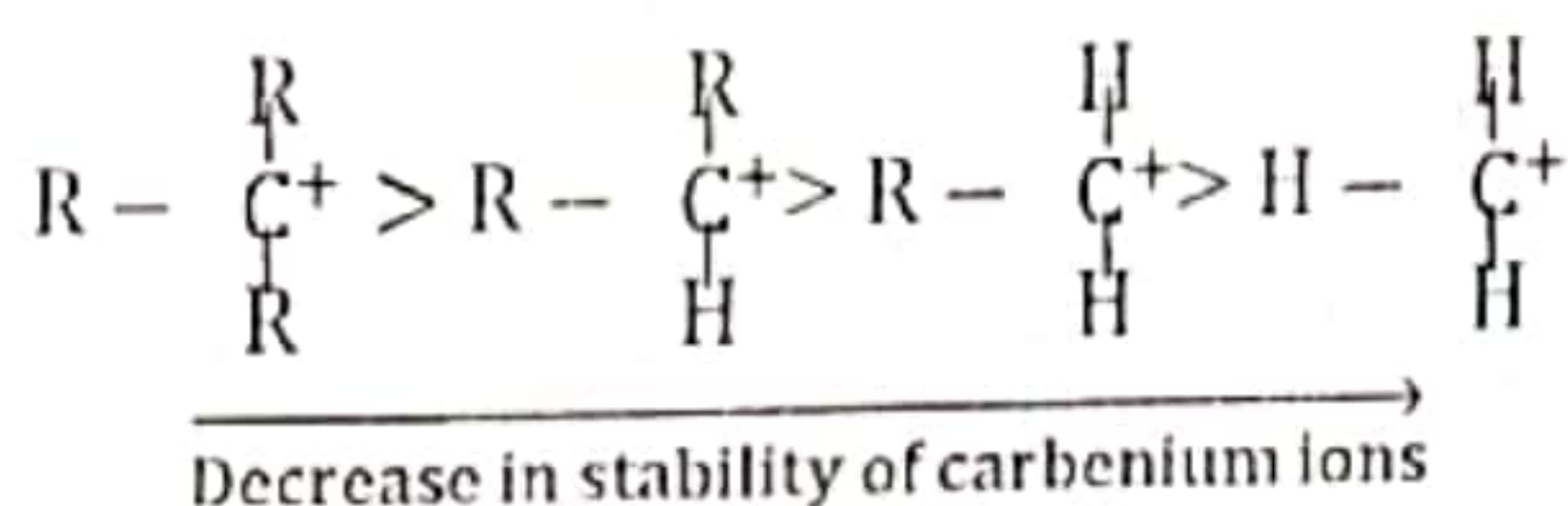
- So 2° carbenium ion receives positive inductive effect from two alkyl groups from two directions. It is stronger positive inductive effect than that received by 1° carbenium ion.

- (iii) **Tertiary (3°) carbenium ion** is the one with three alkyl groups bonded to the positively charged carbon.



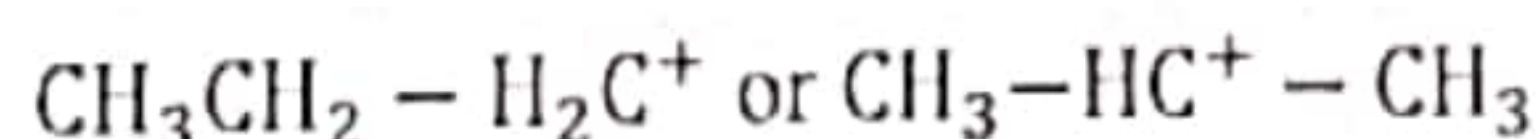
So 3° carbenium ion receives positive inductive effect from three alkyl groups from three directions. It experience strongest positive inductive effect of all classes of carbenium ions.

Therefore stability of different classes of carbenium ions follows the following order:



Example 9

Which one of the following ions is more stable? Explain.



Solution

$\text{CH}_3 - \text{HC}^+ - \text{CH}_3$ is more stable than $\text{CH}_3\text{CH}_2 - \text{H}_2\text{C}^+$ because in $\text{CH}_3 - \text{HC}^+ - \text{CH}_3$, positive inductive effect comes from two directions while in $\text{CH}_3\text{CH}_2 - \text{H}_2\text{C}^+$ positive inductive effect comes from one direction only hence there is stronger +I in $\text{CH}_3 - \text{HC}^+ - \text{CH}_3$ than in $\text{CH}_3\text{CH}_2 - \text{H}_2\text{C}^+$ although both ions have the same number of carbons (equal length of carbon chain).

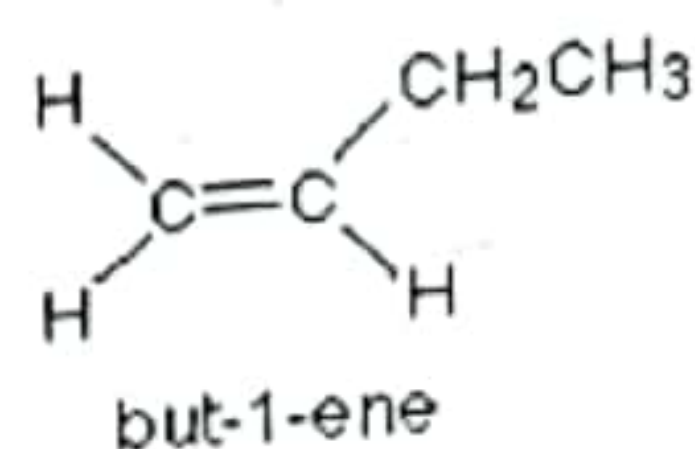
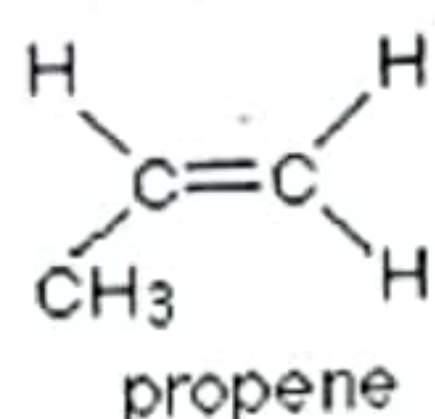
The reader should understand that:

The stability of intermediate carbenium ion is very useful in determining formation of major product in electrophilic addition reaction in unsymmetrical alkene as discussed below.

What is *unsymmetrical* (sometime spelled *asymmetrical*) *alkenes*?

An **unsymmetrical alkene** is the alkene in which the groups or atoms attached to either end of the carbon-carbon double bond are different.

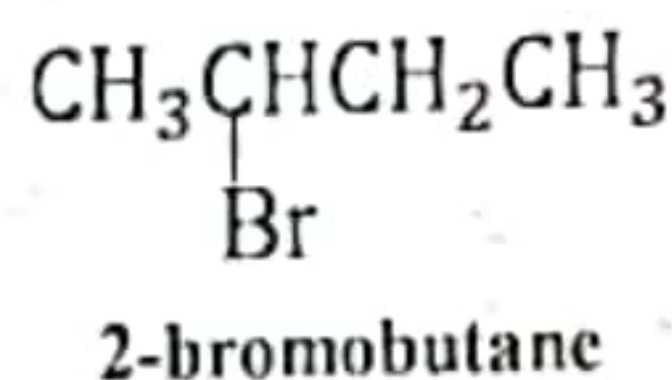
For example, in propene there are hydrogen and a methyl group at one end, but two hydrogen atoms at the other end of the double bond.



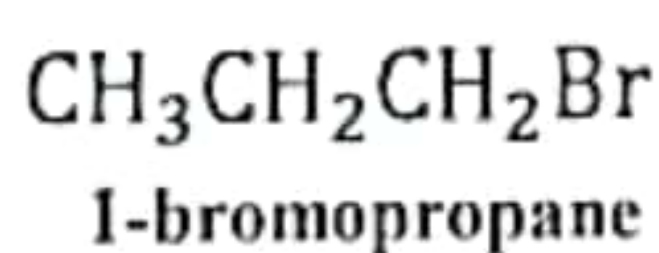
Examples of unsymmetrical alkene

In **symmetrical alkene** (the alkene with the same groups or atoms attached to either end of the carbon-carbon double bond) only one product is formed in electrophilic addition reaction while in unsymmetrical alkenes more than one product is formed. For example:

- $\text{CH}_3\text{CH}=\text{CHCH}_3$ being symmetrical alkene react with HBr to form one product only which is 2-bromobutane.



- $\text{CH}_3\text{CH}=\text{CH}_2$ being unsymmetrical can form two products which are 1-bromopropane and 2-bromopropane.

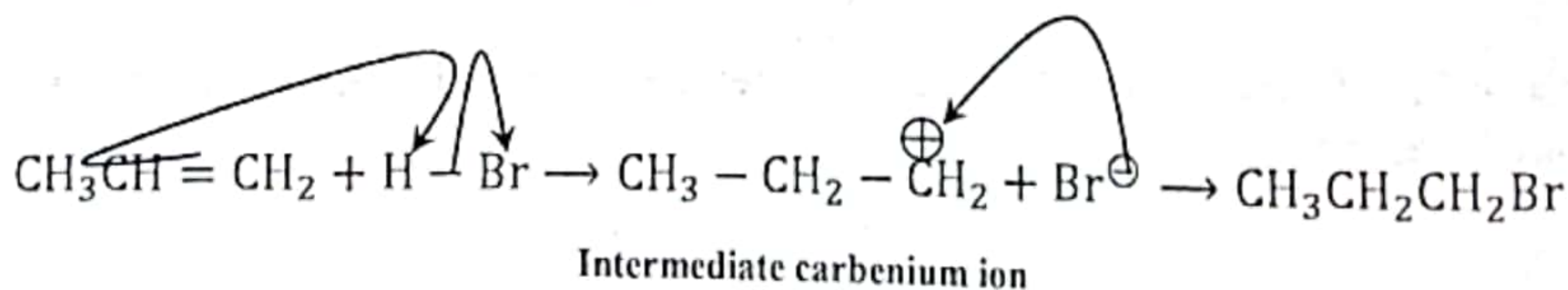


So in electrophilic addition reaction of unsymmetrical alkene, sometimes one of the products is more likely to occur and the product becomes a **major product**. *How the major product is determined?*

- The major product is determined by considering stability of the intermediate carbenium ion.

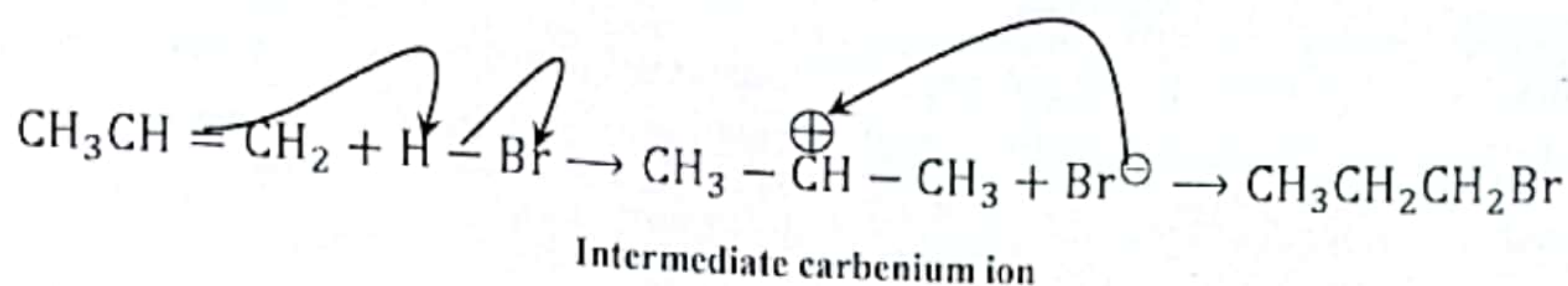
To understand this considers the addition of hydrogen bromide to propene which is electrophilic addition reaction.

1st case: If Br^- adds to the first carbon



In this case the intermediate carbenium ion is primary. It is stabilised by positive inductive effect exerted by one alkyl (ethyl) group from one direction only.

2nd case: If Br⁻ adds to the second carbon



Here the intermediate carbenium ion is secondary. It is stabilised by positive inductive effect exerted by two alkyl (methyl) groups from two directions.

Conclusion:

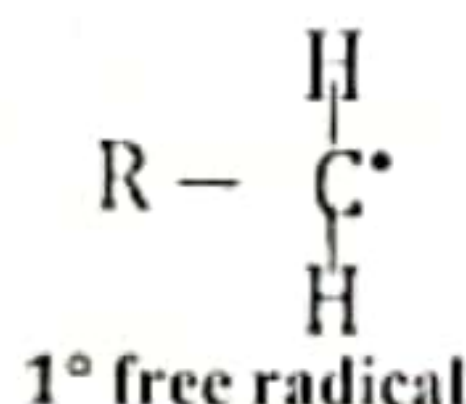
Product formed in the second case is more likely to occur (i.e. it is the major product) because its intermediate carbenium ion is more stable than in the first case as it is stabilised by stronger positive inductive effect. Therefore the correct chemical equation for the reaction between propene and hydrogen bromide becomes:



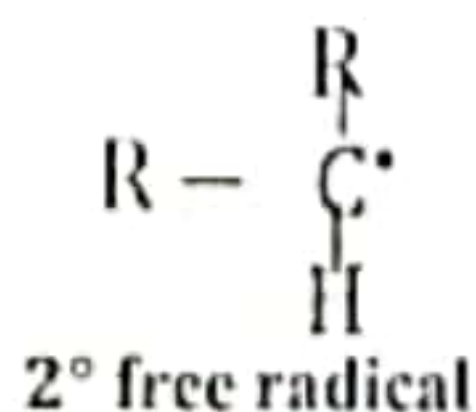
3. Increases stability of free radical

Like carbenium ions, free radicals are electron deficient species. So they need electrons for their stabilisation.

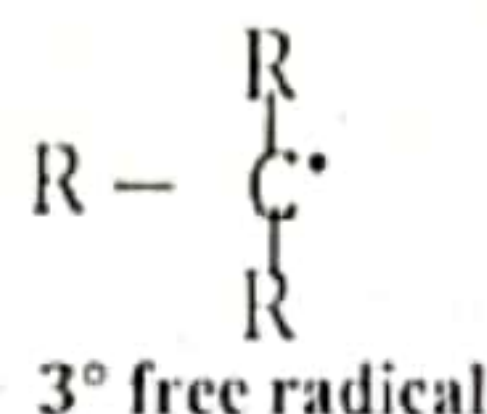
- Therefore trend and reasoning for stability of free radicals is similar to that of carbenium ions. Just replace 'positively charged carbon' with 'carbon with unpaired electron' to derive facts concerning stability of free radicals from facts of stability of carbenium ions. Therefore:
- Stability of free radicals increases with an increase in length of carbon chain due to increase in positive inductive effect in the same trend.
- Like carbanions and carbenium ions, free radicals can be classified as:
 - (i) **Primary (1°) free radical** is the one with only one alkyl group bonded to the carbon with unpaired electron.



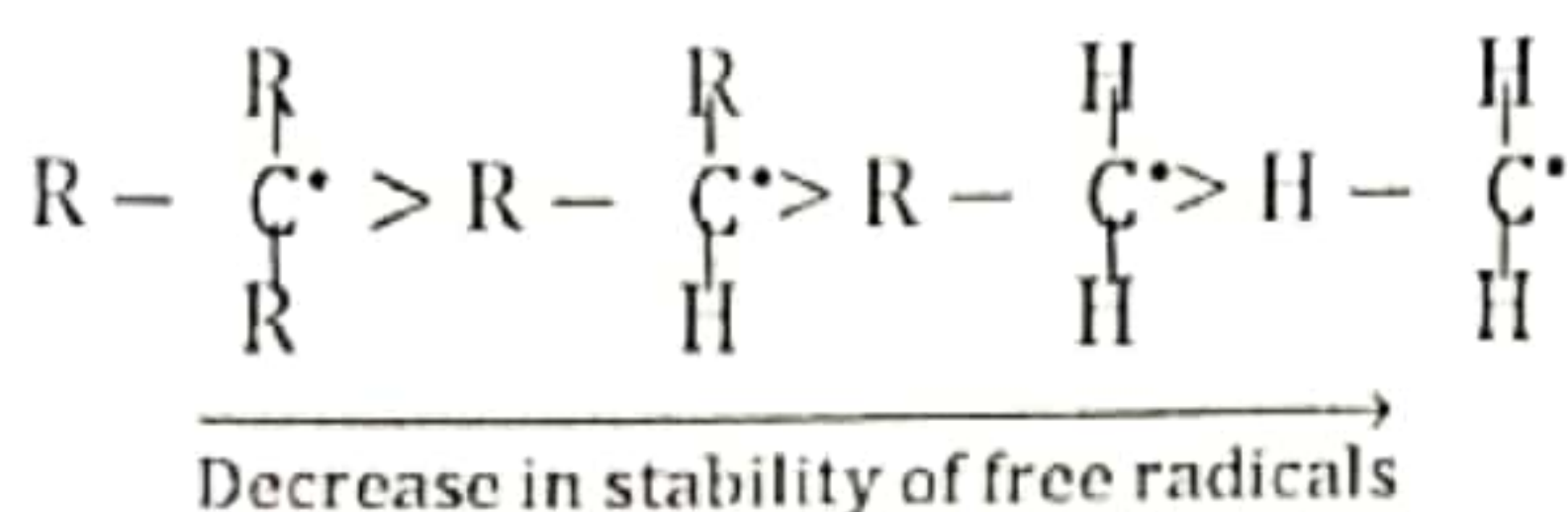
- (ii) **Secondary (2°) free radical** is the one with two alkyl groups bonded to the carbon with unpaired electron.



- (iii) **Tertiary (3°) free radical** is the one with three alkyl groups bonded to the carbon with unpaired electron.



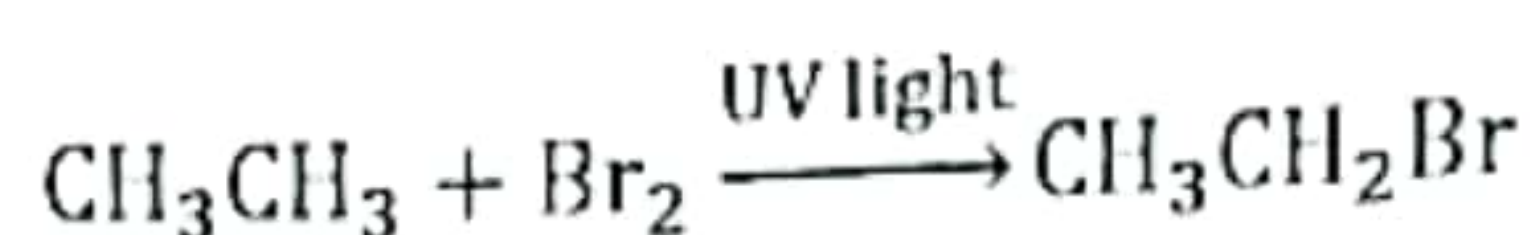
- Stability of different classes of free radicals follows the following order:



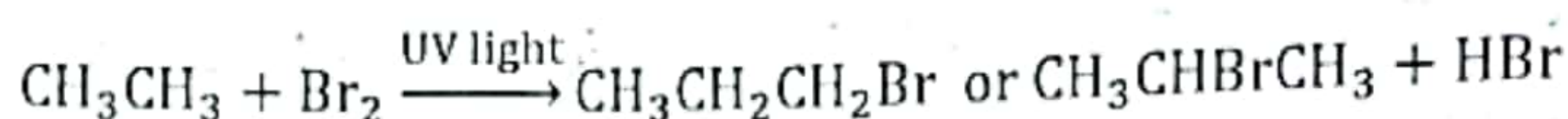
The reader should understand that:

Stability of intermediate free radical brought about by positive inductive effect is very useful in determining major product in monohalogenation of alkane with greater than two carbons as explained below.

- In monohalogenation of methane and ethane there is a possibility of giving only one product while there is a possibility of forming more than one product in monohalogenation of higher members of alkane. For example:
- Monobromination of ethane may give 1-bromoethane only.



- Monobromination of propane may give 1-bromopropane or 2-bromopropane.

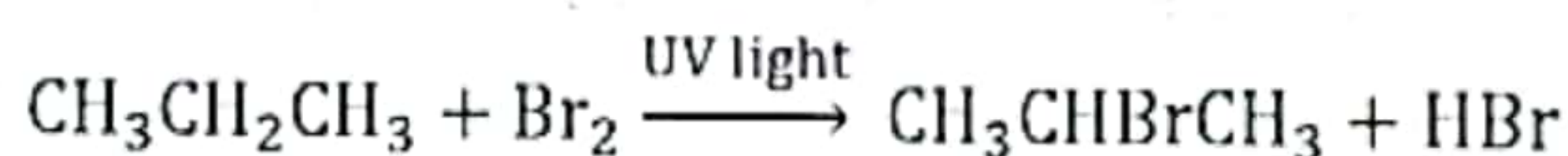


Here:

- If $\text{Br}^\bullet$ substitutes to the primary hydrogen the intermediate free radical becomes $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}$ which is primary free radical.
- If $\text{Br}^\bullet$ substitutes to the secondary hydrogen the intermediate free radical becomes $\text{CH}_3\dot{\text{C}}\text{HCH}_3$ which is secondary free radical.

Since secondary free radical is more stable than primary free radical as it experience stronger positive inductive effect, the secondary hydrogen becomes more reactive favouring substitution in it and hence 2-bromopropane becomes the major product.

- Therefore by writing the major product only, the reaction equation for mono-bromination of propane is;



POSITIVE INDUCTIVE EFFECT AND DEREASE IN ACIDIC STRENGTH OF CARBOXYLIC ACIDS

Positive inductive effect decreases acidic strength of carboxylic acid by:

- Making more difficulty for O-H bond to undergo heterolytic bond cleavage so as release H^+ .
- Making carboxylate ion which is formed after releasing (by difficulty) H^+ from the carboxylic acid unstable.

By making difficulty for O-H bond to break so as to release H^+

Presence of alkyl group which cause +I in carboxylic acid, leads to partial releasing of electrons towards the functional group including O-H bond. This increases electron density in O-H bond which in turn makes O-H bond stronger; and therefore it becomes difficult for the bond to undergo heterolytic bond cleavage so as to release H^+ thus decreasing acidic strength of the acid.

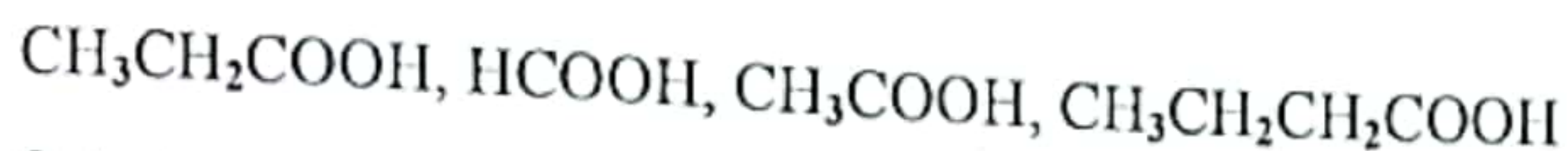
By making carboxylate ion more unstable

Presence of alkyl group (electron releasing group) which cause +I in carboxylate ion formed after releasing (by difficulty) H^+ from carboxylic acid makes the charges in the ion (carboxylate ion) more negative and hence makes the ion unstable (it has low ability of existing on its own without re-combining with H^+) and hence the acidic strength of the carboxylic acid is decreased.

- Generally acidic strength of carboxylic acids decreases with an increase in number of carbons (length of carbon chains) due to increase in positive inductive effect in the same trend.

Example 10

Arrange the following organic compounds in order of decreasing their acidic strength starting with the strongest acid.

**Solution**

- | | |
|-----------------------------|---|
| 1. HCOOH | 3. $\text{CH}_3\text{CH}_2\text{COOH}$ |
| 2. CH_3COOH | 4. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ |

POSITIVE INDUCTIVE EFFECT AND INCREASE IN BASIC STRENGTH OF AMINES

Basic strength of amines depends on the participation of lone pairs of nitrogen in chemical reaction, i.e. if lone pair of electrons can be donated to lewis acid (or H^+) easily then the amine is said to have high basic strength and vice-versa.

Presence of alkyl group which causes positive inductive effect in amines, increases electron density in nitrogen thus making easier for its lone pair to be donated to lewis acid (or hydrogen proton) and hence basic strength of amine is increased.

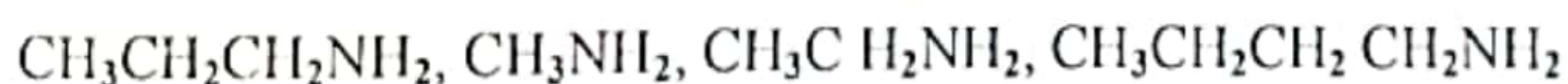
Also positive inductive effect increases basic strength of amine by stabilizing positive charge formed on nitrogen after accepting hydrogen proton (H^+) as result of partial neutralisation of the charge brought about by partial supply of electrons toward the positive charge.

So basic strength of primary amines (amines which formed after replacing only one hydrogen atom of ammonia) increases with an increase of number of carbons (length of carbon chain) as result of increase in positive inductive effect in the same order; e.g. $\text{CH}_3\text{CH}_2\text{NH}_2$ is strong base than CH_3NH_2 .

Also in case of primary amines and secondary amines (amines which are formed when two hydrogen atoms are replaced by two alkyl groups), secondary amine is more basic than primary amines as result of stronger positive inductive effect brought about by two alkyl groups present in the secondary amines. (Basic strength of tertiary amine is complicated by steric hindrance. This will be studied in the section of steric effect)

Example 11

Arrange the following organic compounds in order of their basic strength starting with the weakest base.

**Solution**

- | | | |
|-----------------------------|--|---|
| 1. CH_3NH_2 | 2. $\text{CH}_3\text{CH}_2\text{NH}_2$ | 3. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ |
|-----------------------------|--|---|

MESOMERIC EFFECT

Mesomerism is the movement of an electron pair from one position to another and back again to its original position within the same molecule.

-So **mesomeric effect** occurs in an organic compound as result of movement of an electron pair from one position to another back again to its original position within the same molecule. It occurs in the organic compound as result of mesomerism.

- The spread up of electrons throughout the molecule is known as **delocalisation** of electrons.
- While when electrons are fixed at one position only, those electrons are said to be **localised**

- Negatively charged electrons
- Pi-electrons (electrons in π -bond)
- Lone pair electrons

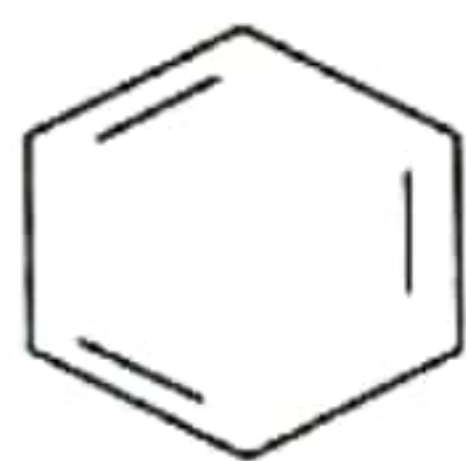
Electrons in sigma (σ) bond can not be involved in mesomerism due to the following reasons:

- ### Conditions for occurrence of mesomerism

- Below is the discussion of those three conditions.

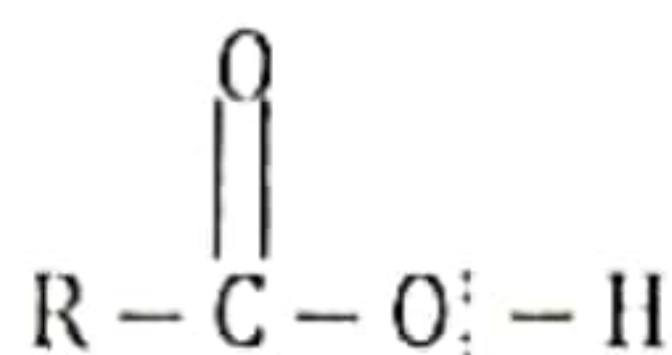
Conjugate state is the alternating of double bond and single bond in the molecule. That is $M = M - M = M - M = M - M$

- According to Kekule (German scientist) structure of benzene can be represented as follows:



(Resonance structure) (Hybrid structure)

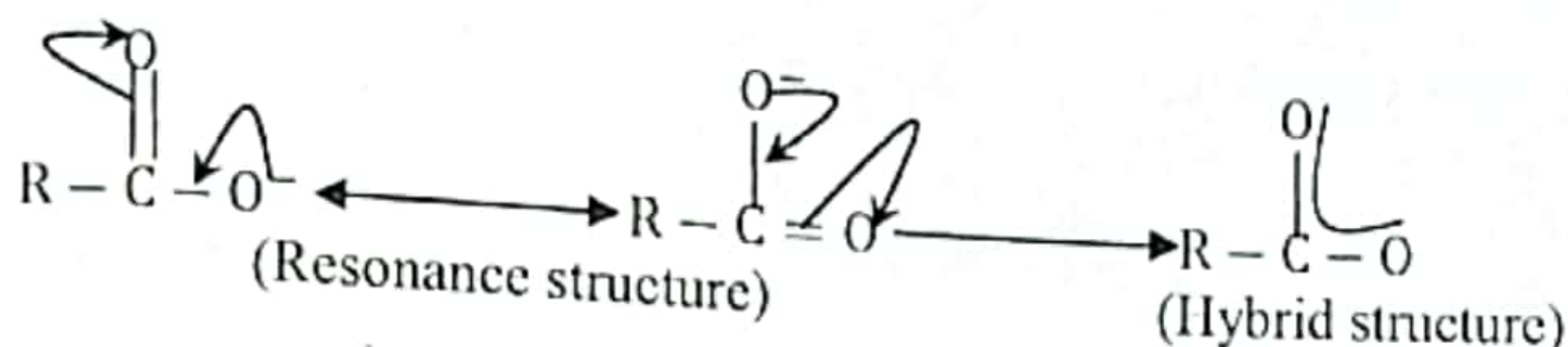
To understand this consider mesomerism in carboxylic acid with the following general molecular structure:



$$\begin{array}{c}
 \text{O} \\
 \parallel \\
 \text{R}-\text{C}-\text{O}^- - \text{H} \longleftrightarrow \text{R}-\text{C}=\text{O}^+ - \text{H} \longleftrightarrow \text{R}-\text{C} \equiv \text{O} - \text{H} \\
 \text{(Resonance structure)} \qquad \qquad \qquad \text{(Hybrid structure)}
 \end{array}$$

(iii) Atom with negative charge must be bonded to another adjacent atom by π -bond

To understand this consider mesomerism in carboxylate ion whose general structure is RCOO^- .



TYPES OF MESOMERIC EFFECT

Like inductive effect, mesomeric effect can be divided into:

- Negative mesomeric effect ($-M$) and
- Positive mesomeric effect ($+M$)

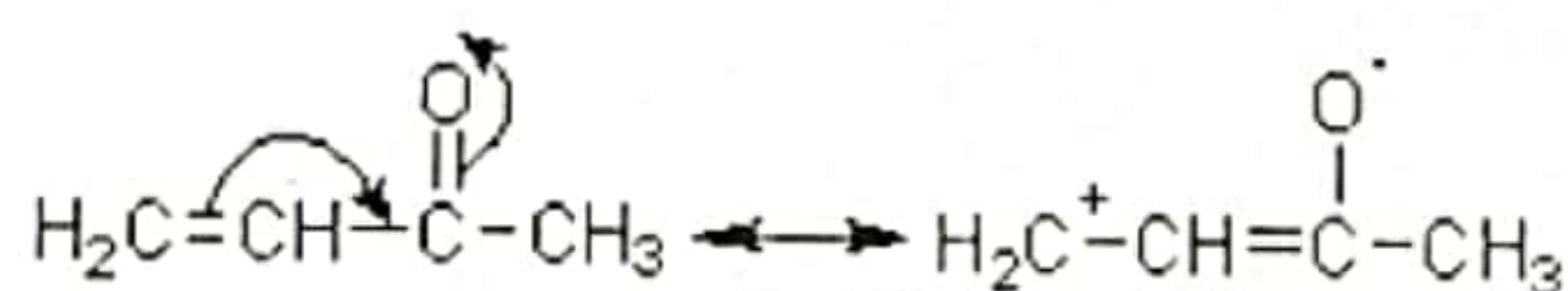
Negative mesomeric effect is the one shown by substituents or groups that withdraw electrons by delocalization mechanism from rest of the molecule.

- It occurs when the atom with lone pair in the substituent is directly bonded to another atom by π (pi) bond. In other words; it occurs if the atom with lone pair in the substituent has double or triple bond.

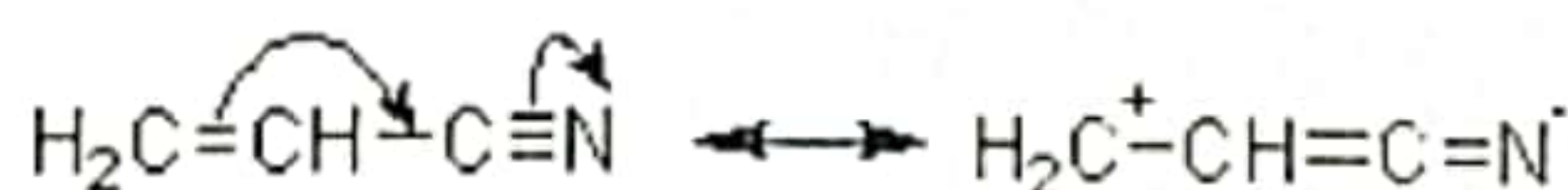
The electron density on rest of the molecular entity is decreased due to this effect.

- To have better understanding on negative mesomeric effect, consider the following three illustrations:

First illustration: Negative mesomeric effect of carbonyl group.



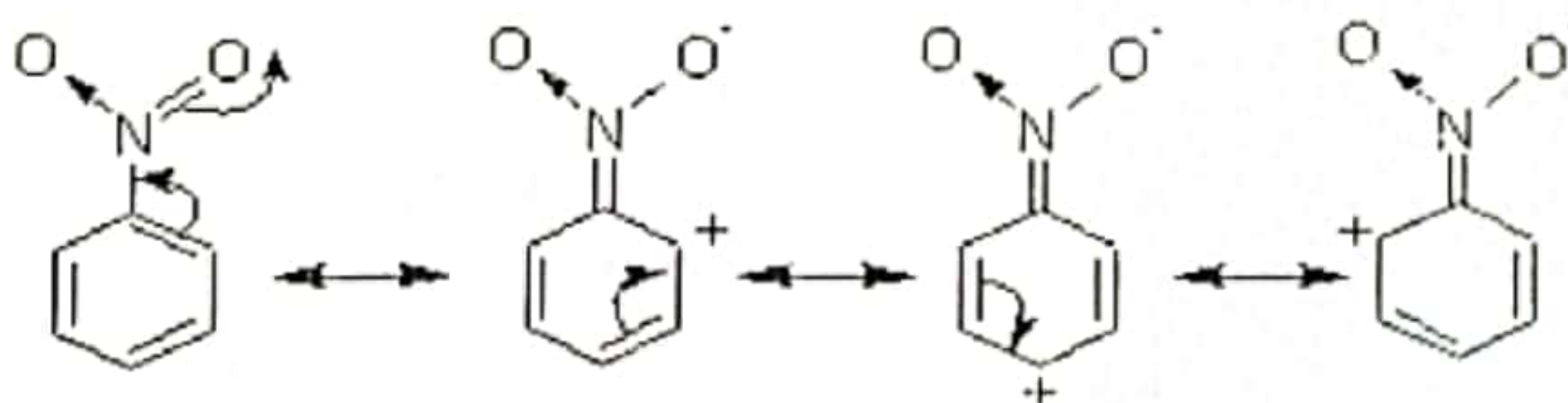
From the above illustration, it is clearly understood that the carbonyl group withdraws electrons by delocalization of π electrons and reduces the electron density particularly on the third carbon.



Second illustration: Negative mesomeric effect of cyano group.

Here the cyano group withdraws electrons by delocalization of π electrons and reduces the electron density particularly on the third carbon.

Third illustration: Negative mesomeric effect of nitro group.



Here the nitro group withdraws electrons by delocalization of conjugated π electrons and reduces the electron density particularly on the second and fourth carbon.

That is about negative mesomeric effect, what about positive mesomeric effect?

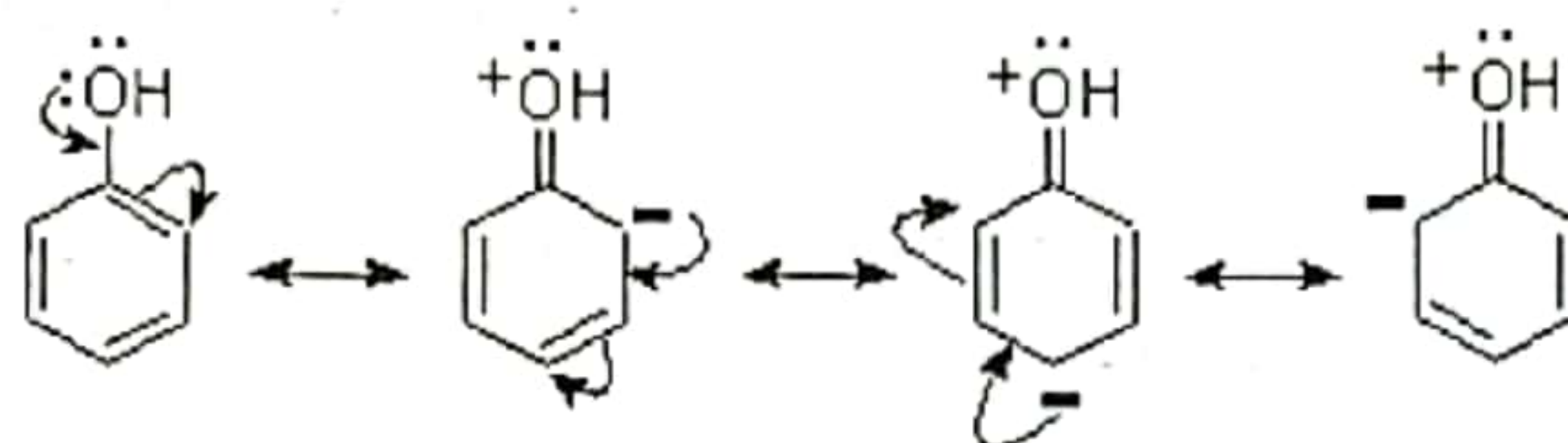
Positive mesomeric effect is the one shown by substituents or groups that release electrons by delocalization mechanism to rest of the molecule.

- It occurs when the atom with lone pair in the substituent is directly bonded to another atom by σ (sigma) bond. In other words; it occurs if the atom with lone pair in the substituent has single bonds only.

The electron density on rest of the molecular entity is increased due to this effect.

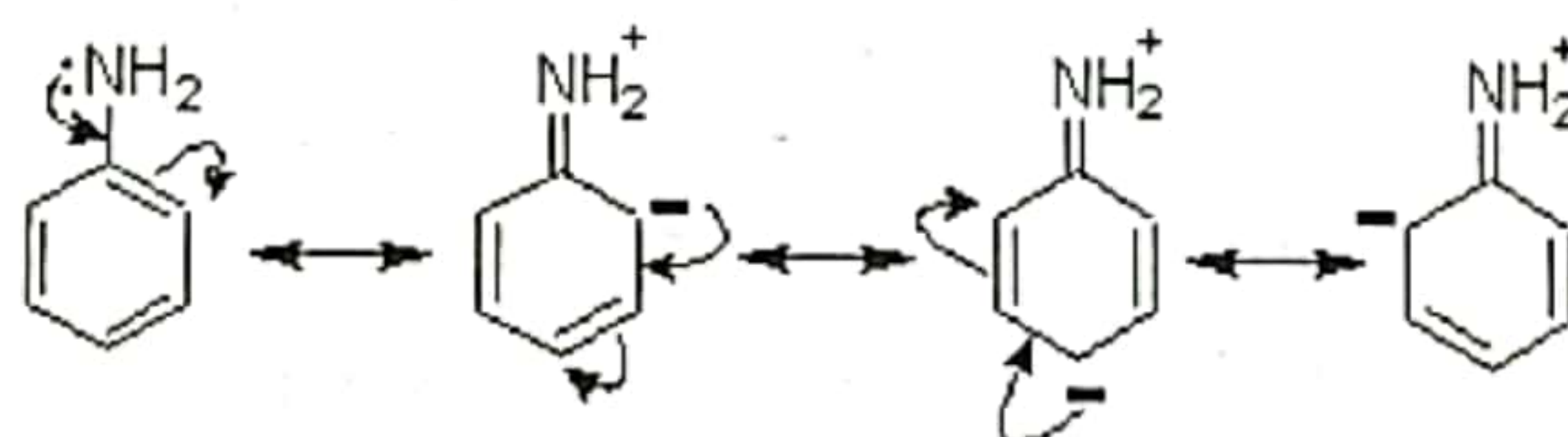
- To have better understanding on positive mesomeric effect, considers the following two illustrations:

First illustration: Positive mesomeric effect of hydroxyl group.



From the above illustration, it is clearly understood that the hydroxyl group releases electrons by delocalization of lone pair electrons towards the ring and increases the electron density particularly on the second and fourth carbon.

Second illustration: Positive mesomeric effect of amino group.



Here the amino group releases electrons by delocalization of lone pair electrons towards the ring and increases the electron density particularly on the second and fourth carbon.

Effect of mesomeric effect on mechanism of organic reaction

1. Stabilises pi bond

Usually pi bond are very reactive and in most cases a molecule with pi bond tends to undergo addition reaction.

- But this is only true when the bond is localised like in simple alkene and alkyne.

When pi bond is delocalized in mesomerism, the bond becomes stable and difficult to break in doing addition reaction because extra energy is required to break the resonance of electrons before breaking the bond.

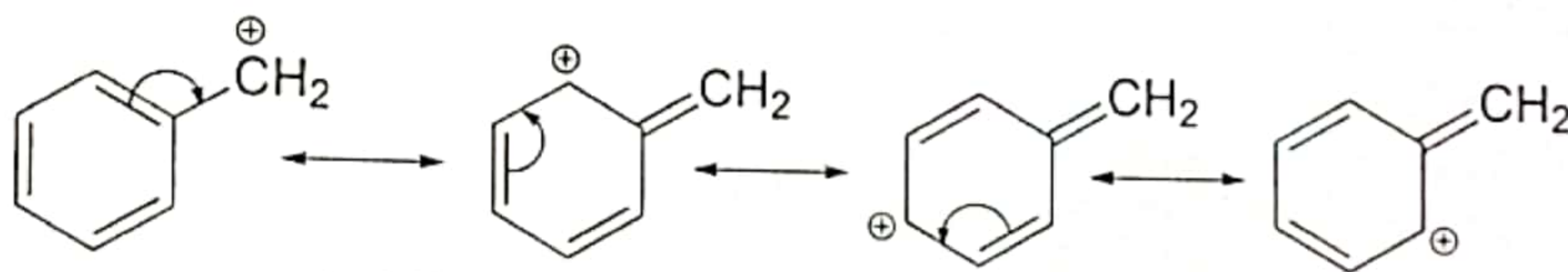
- The delocalisation of pi electrons in the mesomerism explains why benzene does not undergo addition reaction easily although it is highly unsaturated. The situation is different to simple alkenes and alkynes where the pi bonds are localised and therefore they undergo addition reaction readily.

2. Stabilises ions

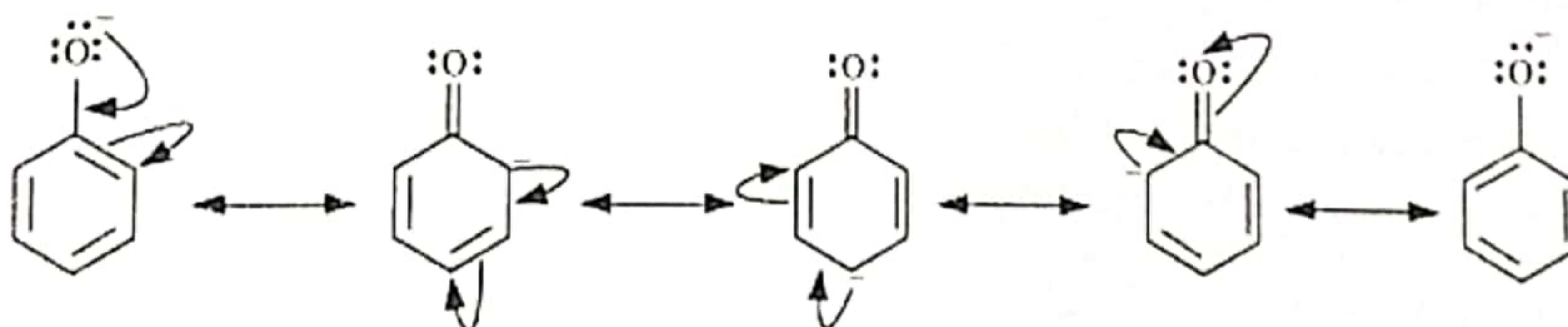
"Nature hates localized charges." That is the general rule for stability of an ion, whether it is either positively or negatively charged.

- In other words if a molecule must have a charge, it is better to have the charge distributed over as many atoms as possible through several ways including mesomerism (resonance).
- In addition, when given the choice, it is better to have more negative charge on a more electronegative atom (e.g. O), and more positive charge on a less electronegative atom (e.g. C).

Mesomerism stabilises both cations and anions by enabling delocalisation of positive charge and negative charge respectively throughout the molecule. (See illustrations below)



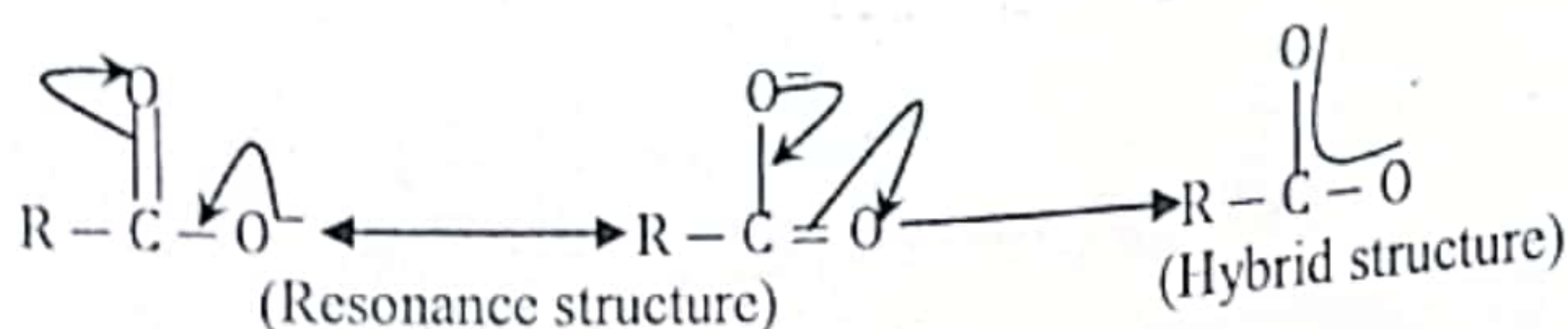
Stabilisation of positive charge ion by mesomerism



Stabilisation of negative charge ion by mesomerism

If the molecule has greater number of strong electronegative atoms which shares negative charge in the mesomerism, the ion then become more stable.

- For example, carboxylate ion with two oxygen atoms is more stable than phenoxide ion for this reason.



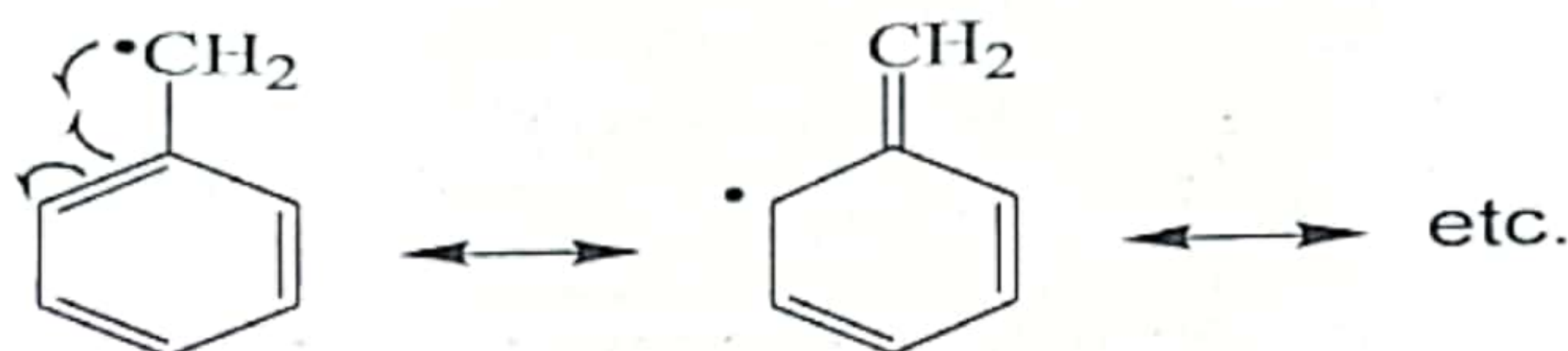
3. Stabilises free radicals

Again here there is another general rule; *"Nature hates unpaired electrons."*

- If a molecule must have an unpaired electron (free radical), it is better to have the unpaired electron distributed over as many atoms as possible through several ways like mesomeric and inductive effects.

Mesomerism stabilises free radicals in similar manner to stabilisation of ions as explained earlier.

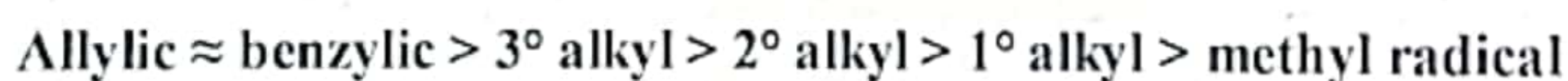
- Resonance stabilisation of allylic and benzylic free radicals is illustrated below.



The reader should understand that:

Resonance stabilisation (involves total movement of electrons) of organic intermediates is greater than stabilisation by inductive effect (involves partial movement of electrons).

- For example, stability of common organic free radicals is according to the following order:



Where stability of allylic and benzylic free radicals is determined by mesomerism while the stability of alkyl groups is determined by positive inductive effect

STERIC EFFECT

Whenever a chemical reaction between two compounds takes place, directly or indirectly it results in the formation of bond between the atoms of these two compounds.

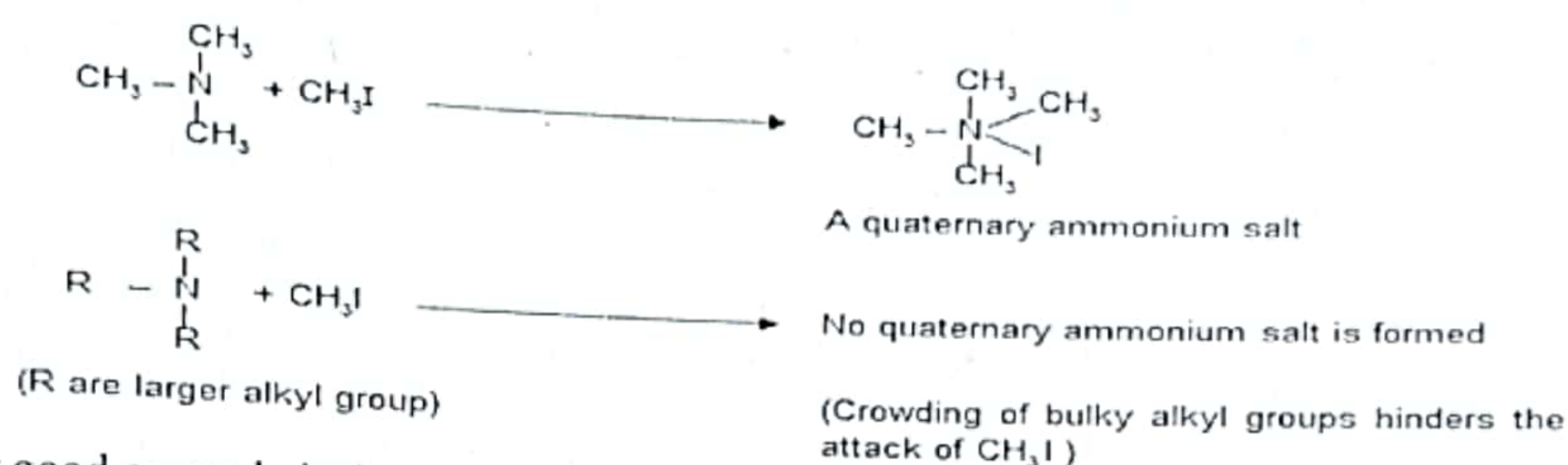
- The bonding atoms of the two reacting compounds are, in fact, the active centres.
- These will react (form the bond) with one another only if they come with in contact of each other.
- If we surround one of them with such mass of other atoms or groups that the other reacting atom is unable to force its way in, the reaction may not at all take place or may take place only slowly. Such a hindrance due to spatial crowding (crowding a space) is called **steric hindrance**. *Steric hindrance occurs when the large size of groups within a molecule prevents chemical reactions that are observed in related molecules with smaller groups.*

However, the spatial crowding may not always hinder a reaction; sometimes it may facilitate a reaction. It is often exploited to change the reactivity pattern of a molecule by stopping unwanted side-reactions (**steric protection**).

- Therefore, the term **steric effect** is better than the term steric hindrance.

Steric effect may be defined as *modification in molecular properties resulting from a spatial crowding of a reacting atom in a molecule*. A good example of steric effect is discussed below:

- The tertiary amine with the name trimethylamine reacts with methyl iodide to form a quaternary salt tetramethyl ammonium iodide, but if the alkyl groups in tertiary amine are large, it does not react with methyl iodide and so, does not form the quaternary ammonium salt :



Another good example is that of esterification between a carboxylic acid and an alcohol. Bulkier the alkyl group in acid or alcohol, slower is esterification.

The student should understand that:

Because the reactivity of free radicals decreases as steric hindrance increases, steric hindrance is said to increase stability of free radical.

STERIC EFFECT AND DECREASE OF BASIC STRENGTH IN TERTIARY AMINES

Amine not only donates its lone pair to Lewis acid but also welcomes the Lewis acid to bond with nitrogen of the amine.

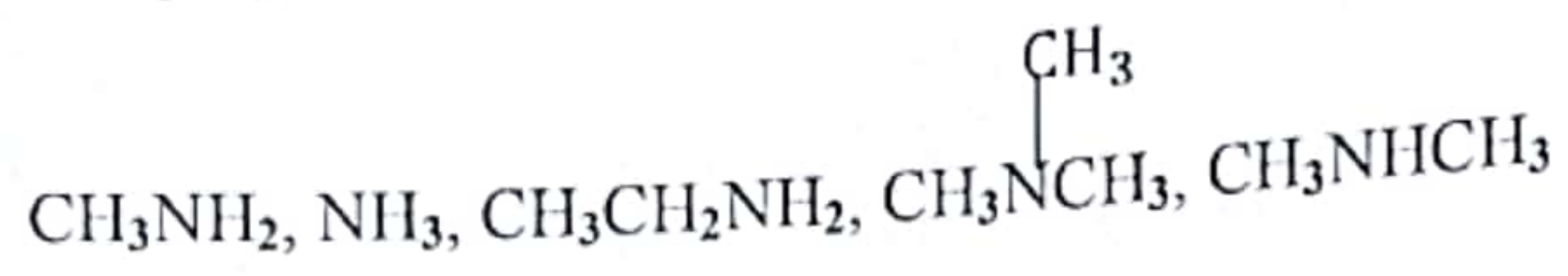
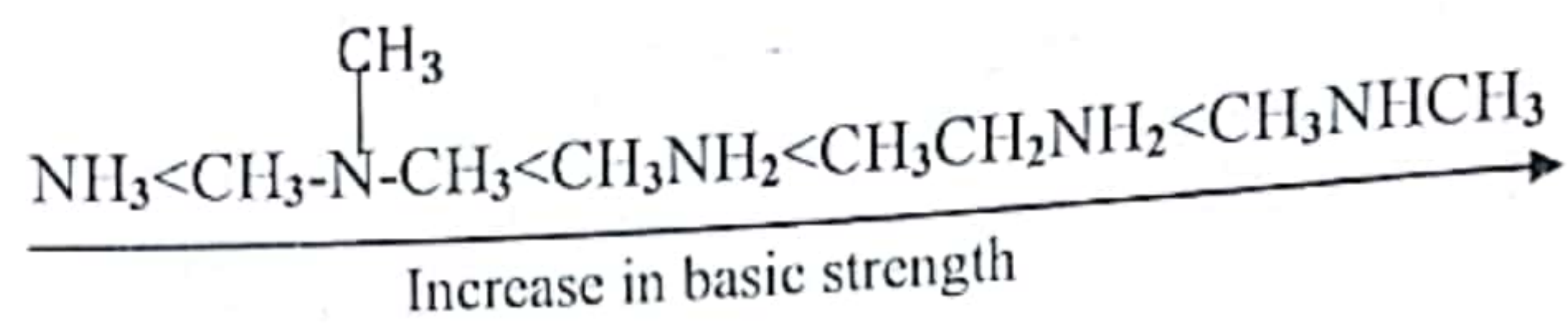
- Inductive effect studied earlier dealt with the ability of the amine to donate its lone pair.
- However amine with greater electron density may become weaker base if its nitrogen is overcrowded with groups of carbons thus making difficult for it to bond with Lewis acid. This is steric effect.
- So steric effect (specifically steric hindrance) is the one which determines the ability of amine to allow Lewis acid to bond with its nitrogen.

Steric hindrance is significantly experienced when the nitrogen is surrounded with bulky groups. A clear example of this is in tertiary amines (amine which is formed after replacement of all three hydrogen atoms of ammonia by alkyl groups).

- Although there is strongest positive inductive effect in tertiary amines, unexpectedly tertiary amine is least basic (weakest base) among three classes of amines (primary, secondary, and tertiary amines) because there is large steric hindrance for Lewis acid, e.g. H^+ to bond to the nitrogen atom of amine because the atom (nitrogen atom) is overcrowded with the three alkyl groups.

Example 12

Arrange the following organic compound in order of increasing in their basic strengths.

**Solution**

PRACTICE EXERCISE 6

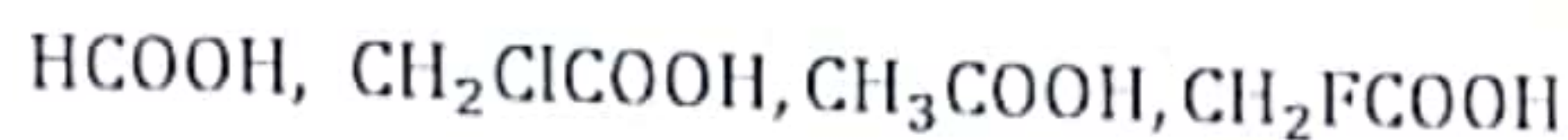
Problem 1

Account for the following:

- Although H_3C^- and NH_3 are isoelectronic, the former is stronger nucleophile.
- $\text{CH}_2\text{ClC}\equiv\text{C}^-$ is more stable than $\text{CH}_3\text{C}\equiv\text{C}^-$
- H_2O is stronger acid than CH_3OH
- CH_3NH_2 is stronger base than NH_3
- Although nitrogen in tertiary amine experience stronger positive inductive effect than nitrogen in secondary amine, the later is stronger base than the former.
- Esterification between butanoic acid and butanol occurs at slower rate than esterification between ethanoic acid and ethanol.

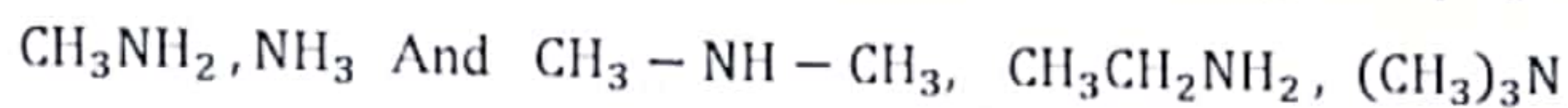
Problem 2

Arrange the following organic compounds in order of increasing their basic strength.



Problem 3

Arrange the following compounds in order of increasing their pK_b values.



Problem 4

Between NH_3 and NH_2OH which one has greater K_a value? Give a reason for your choice.

Problem 5

Alkenes, alkynes and benzene are all unsaturated hydrocarbon. However benzene does not undergo addition while alkene and alkynes do. Explain.

Chapter 7

ISOMERISM IN ORGANIC COMPOUNDS

Literally the word 'isomer' comes from two Greek words; 'isos', which means equal and 'meros', which means parts.

By definition, **isomerism** is the existence of compounds with the same molecular formula but differ in their structures or spatial arrangement of atoms in space.

- On another hand, **isomers** are compounds with the same molecular formula but differ in their structures or spatial arrangement of atoms in space.

Isomers or isomerism can be grouped into two types which are:

- i. Structural /constitutional isomers (or isomerism)
- ii. Stereo isomers(or isomerism)

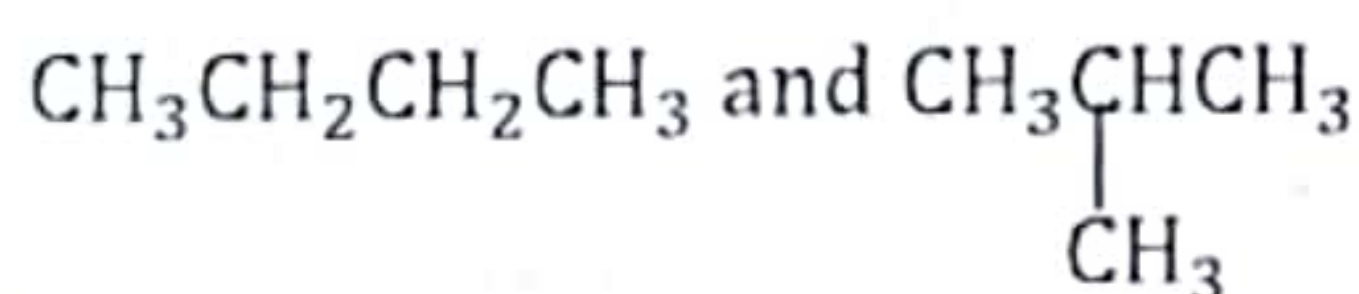
STRUCTURAL ISOMERS

Structural isomers are compounds with the same molecular formula but differ in their structures.

- Structural isomers can further divided into three types;
 - chain isomers
 - Position isomers
 - Functional isomers
 - Metamers

Chain isomers

These are organic compounds with the same molecular formula, the same functional group but differ in their parent chain. For example;

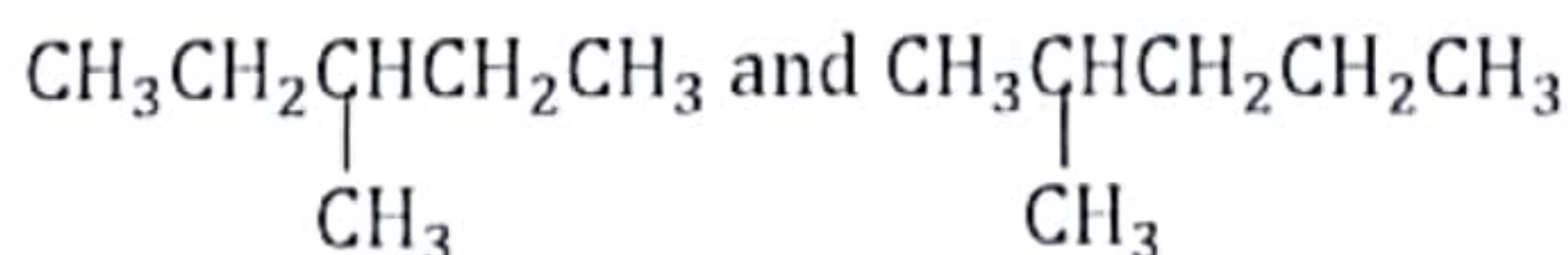


Are chain isomers with the same molecular formula but they differ in their parent chain, the first compound with four carbons and the second one with three carbons (in the parent chain)

- Chain isomers are also known as **skeletal** or **nuclear isomers**.

Position isomers

These are organic compounds with the same molecular formula, the same parent chain, the same functional group but differ in position of substituents or functional groups. For example:



Are position isomers with the same molecular formula of C_5H_{12} , the same parent chain of 5 carbons, the same functional group of alkane but in the first compound $-\text{CH}_3$ is at third carbon while in the second one the group ($-\text{CH}_3$) is attached at the second carbon.

Other examples are:

- $\text{CH}_3\text{CH}=\text{CHCH}_3$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
- $\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{OH} \end{array}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Functional isomers

These are organic compounds with the same molecular formula but differ in their functional groups. For example;

- $\text{CH}_3\text{CH}=\text{CH}_2$ and $\triangle$ are functional isomers with the same molecular formula of C_3H_6 ; but the first compound is alkene while the second one is alkane(cycloalkane).
- Always **aliphatic alkenes and cycloalkanes with equal number of carbons are functional isomers.**
- CH_3OCH_3 and $\text{CH}_3\text{CH}_2\text{OH}$ are functional isomers with the same molecular formula of $\text{C}_2\text{H}_6\text{O}$; but the first compound is ether while the second one is alcohol.
- Always **ethers and alcohols with equal number of carbons are functional isomers.**
- $\text{CH}_2=\text{C}=\text{CH}_2$ and $\text{CH}_3\text{C}\equiv\text{CH}$ with the same molecular formula of C_3H_4 ; but the first compound is alkene (diene) while the second compound is alkyne.

It should be noted that:

When functional isomers are in equilibrium to each other the new type of isomerism rise which is known as **tautomerism**. A good example of this is enol-ketol tautomerisation explained earlier in the rearrangement reaction.

Metamers

Metamerism arises when different alkyl groups are attached to the same functional group.

- **Metamerism is the type of isomerism is due to the difference in the nature of alkyl groups attached to the polyvalent atom of the functional group.**
- So **metamers are organic compounds in the same homologous series with the same molecular formula but differ in the nature of alkyl groups attached to polyvalent atom of the functional group.**

Compounds like ethers and amines show metamerism. For example:

- (i) $\text{CH}_3-\text{NH}-\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_3$ are metamers
- (ii) $\text{CH}_3-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ are metamers

STEREO ISOMERS

Stereo isomers are compounds with the same molecular formula and structure but they differ in spatial arrangement of atoms in space.

- Stereo isomers can further divided into two types which are:

- Geometric isomers
- Optical isomers

Geometric isomers

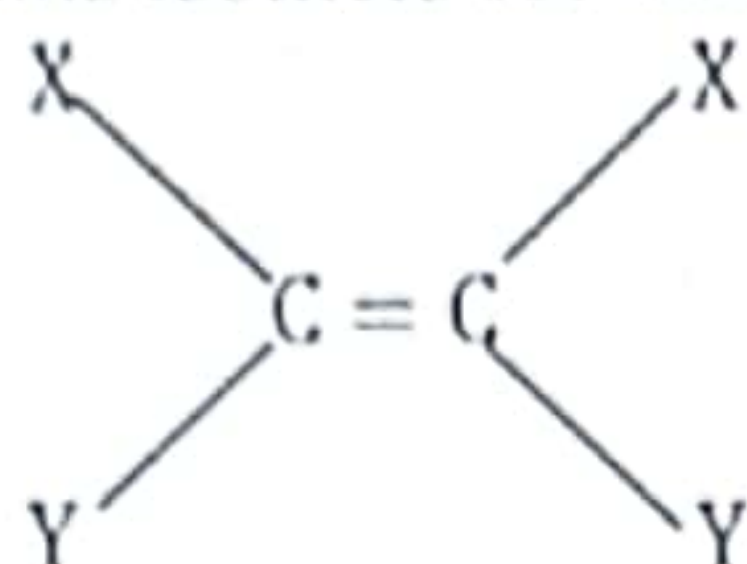
Geometric isomers compounds with the same molecular formula and structure but they differ in arrangement of groups with respect to position of unrotated bond.

- Conditions which favour occurrence of geometric isomers are;
 - If there is no free rotation of carbon atoms like in $\text{C}=\text{C}$ of alkene or cyclic alkane.
 - Carbons in unrotated bond must be bonded to two different groups.

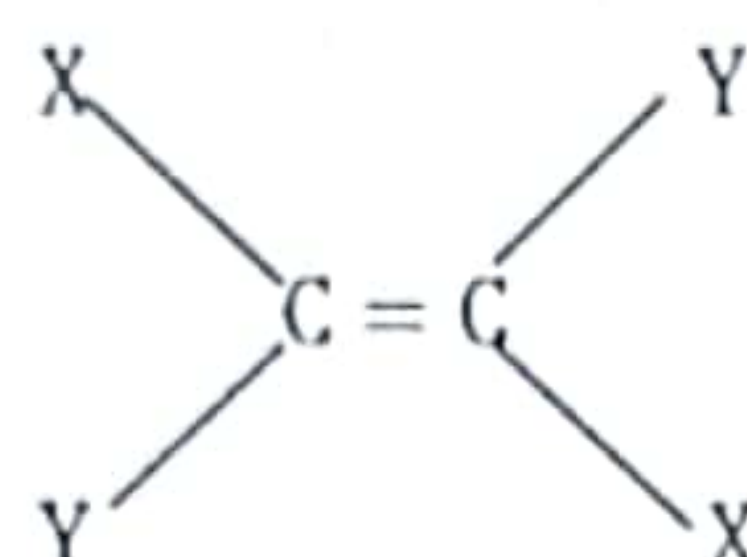
Geometric isomers can further be divided into **cis-isomers** and **trans-isomers** and therefore are also known as **cis-trans isomers**.

- **Cis** comes from Latin means **the same side** while another Latin word **trans** means **opposite side** or **across from**.

General form of cis-trans isomers for alkene can be represented as follows:

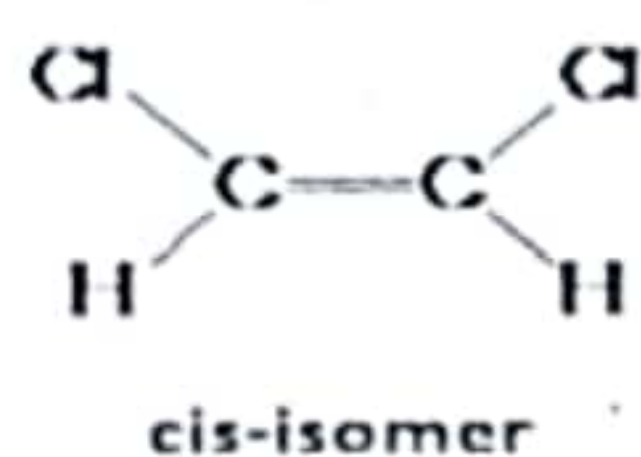
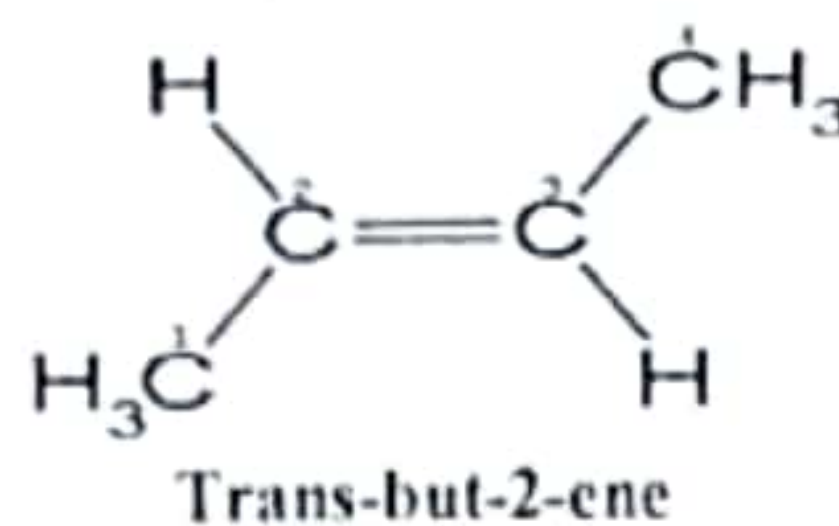
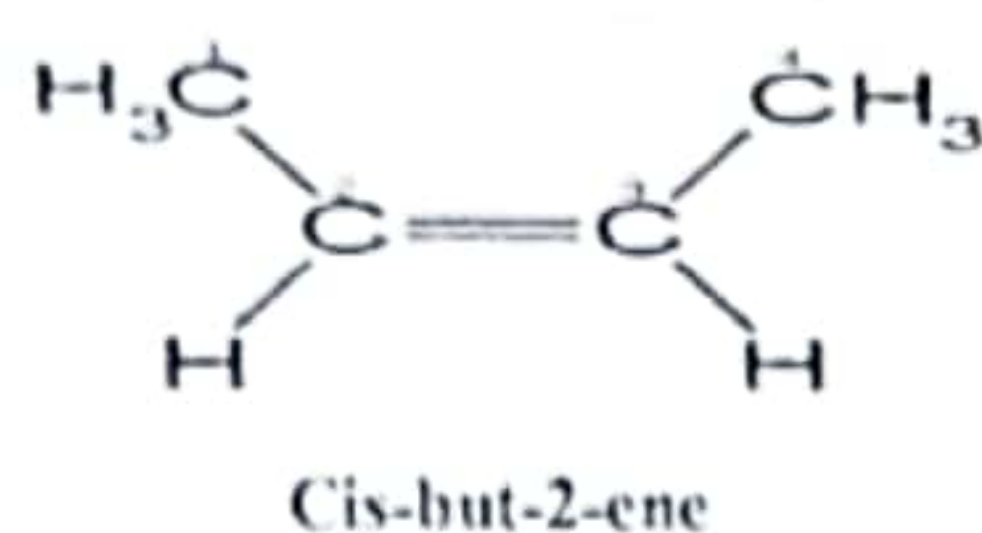


Cis-isomer (the same substituents are in the same side with respect to position of double bond).

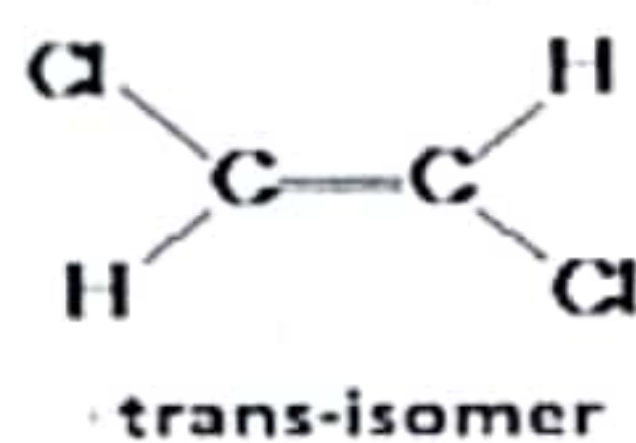


Trans-isomer (the same substituents are in opposite side with respect to position of double bond).

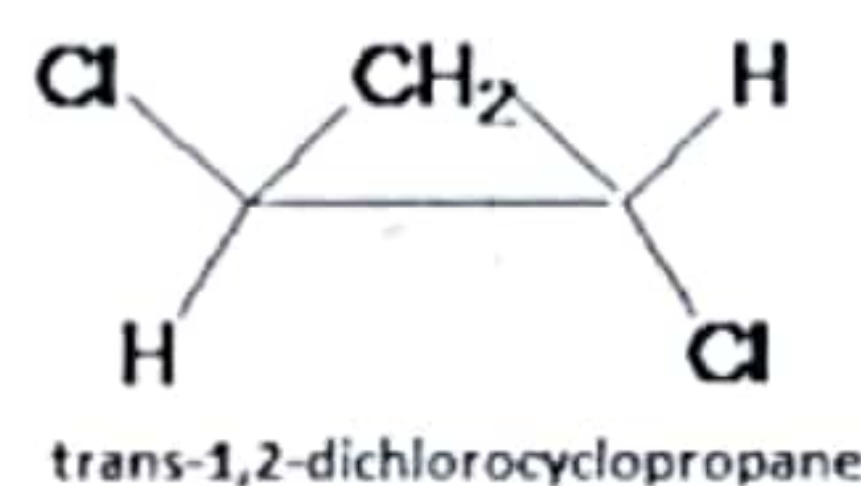
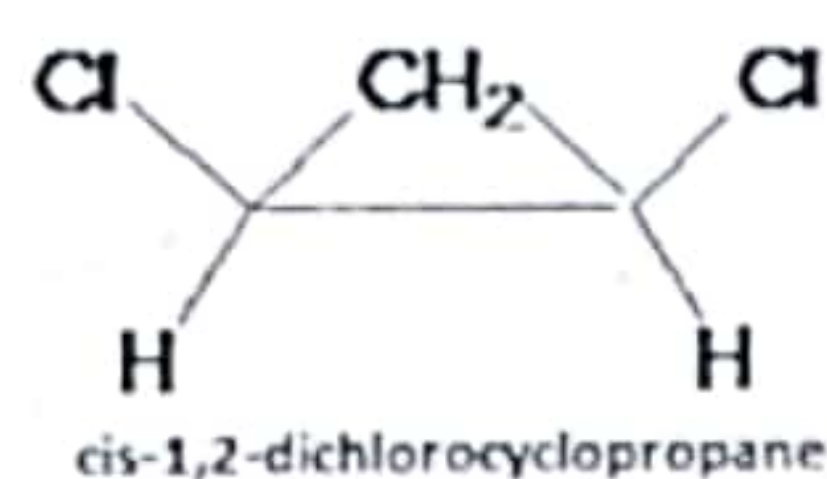
Examples of geometric isomers are;



(cis-1,2-dichloroethane)



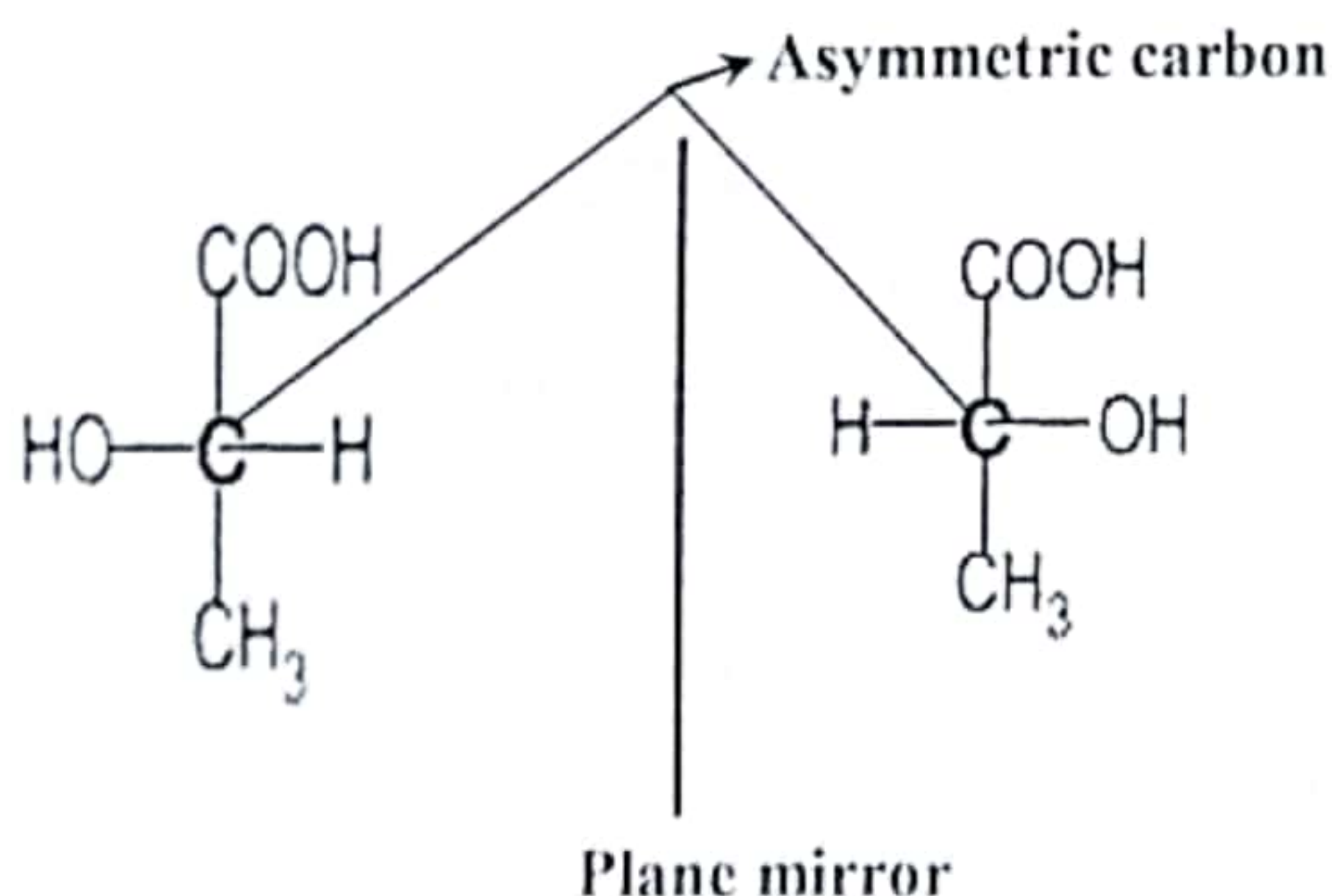
(trans-1,2-dichloroethane)



Optical isomers

Optical isomers are stereoisomers that are mirror image of each other.

- Optical isomers are also known as **enantiomers**. Optical isomers can occur when there is an **asymmetric carbon** atom. An asymmetric carbon atom is one which is bonded to **four different** groups.



A detailed discussion of optical isomers is beyond the scope of this book.

PRACTICE EXERCISE 7

Problem 1

Define the following terms:

- i. Stereo isomers
- ii. Cis-isomer
- iii. Trans –isomer
- iv. Metamerism
- v. Metamers
- vi. Geometric isomerism
- vii. Skeletal isomerism
- viii. Position isomerism
- ix. Functional isomerism

Problem 2

Write structure of all functional isomers of the compound with compound with the following molecular formula.

- i. C_3H_4
- ii. C_2H_6O

Problem 3

Give structures of all metamers of the compound with the following molecular formula.

- i. $C_5H_{13}N$
- ii. $C_5H_{12}O$

Problem 4

Draw structures of possible geometric isomers of the compound with the molecules formula of C_6H_{12}

Problem 5

Give structures of all possible position isomers of the compound with the molecules of formulas of $C_5H_{10}O$.

Chapter 8

MOLECULAR FORMULA DETERMINATION FOR ORGANIC COMPOUNDS

EMPRICAL AND MOLECULAR FORMULA

Empirical formula is the chemical formula which gives simplest ratio of number of atoms present in a molecule.

Molecular formula is the chemical formula which gives exact number of each atom present in a molecule.

Example 1

An organic compound has molar mass of 150g/mol and contains 72%carbon, 6.67% hydrogen and 21.33%oxygen. What is empirical and molecular formula of the compound?

Solution

Constituents atoms	C	H	O
Percentage composition of each	72	6.67	21.33
Mass of each in 100g of the compound	72g	6.67g	21.33g
Number of moles of each, Using $n = \frac{m}{M_r}$	$\frac{72g}{12g\text{mol}^{-1}}$ = 6mol	$\frac{6.67g}{1g\text{mol}^{-1}}$ = 6.67mol	$\frac{21.33g}{16g\text{mol}^{-1}}$ = 1.33mol
Divide by smallest to get Simpler ratio	$\frac{6\text{mol}}{1.33\text{mol}}$ = 4.5mol	$\frac{6.67\text{mol}}{1.33\text{mol}} = 5\text{mol}$	$\frac{1.33\text{mol}}{1.33\text{mol}} = 1$
Multiply by 2 throughout to get simplest ratio	9	10	2

Hence empirical formula for the compound is $\text{C}_9\text{H}_{10}\text{O}_2$

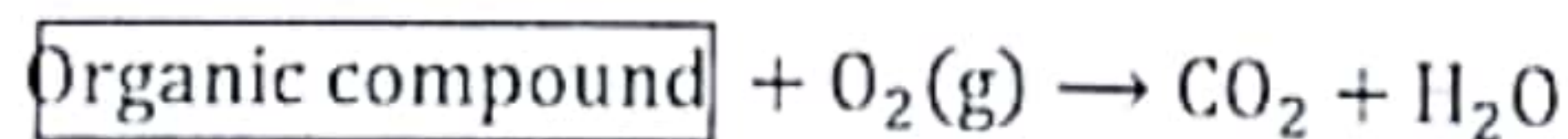
Let Molecular formula be $(\text{C}_9\text{H}_{10}\text{O}_2)_n$

Then $108n + 10n + 32n = M_r$; $150n = 150$ or $n = 1$

Hence molecular formula of the compound is $\text{C}_9\text{H}_{10}\text{O}_2$

DETERMINATION OF MOLECULAR FORMULA OF ORGANIC COMPOUNDS BY COMBUSTION

Most of organic compounds combust in oxygen to yield carbondioxide and water;



The technic behind determination of composition of the organic compound by this method depends on whether the compound is hydrocarbon or substituted hydrocarbon with oxygen.

For substituted hydrocarbon with oxygen only:

If $\text{C}_x\text{H}_y\text{O}_z$ represent the substituted hydrocarbon then the skeleton (unbalanced) equation for its combustion become: $\text{C}_x\text{H}_y\text{O}_z + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

From the above equation it is clearly understood that:

- The whole mass of carbon, C, in the product side must come from $\text{C}_x\text{H}_y\text{O}_z$ and hence;

$$\text{mass of C in } C_xH_yO_z = \text{mass of C in } CO_2$$

- The whole mass of hydrogen, H, in the product side must come from $C_xH_yO_z$ and hence;

$$\text{mass of H in } C_xH_yO_z = \text{mass of H in } H_2O$$

- The mass of oxygen in the product side (O in CO_2 and H_2O) comes from $C_xH_yO_z$ and oxygen gas used for combustion in the reactants side. So amount of oxygen in $C_xH_yO_z$ cannot be determined directly. However if the total mass of $C_xH_yO_z$ combusted is known the amount of oxygen can be determined indirectly by using either of the following facts:

- **Total mass of $C_xH_yO_z$ = mass of C + mass of H + mass of O**

From which:

$$\text{Mass of O} = \text{mass of C} + \text{mass of H} - \text{total mass of } C_xH_yO_z$$

- **Total percentage of all atoms in $C_xH_yO_z$ = 100%**

From which:

$$\text{Percentage of O} = 100\% - (\% \text{ of C} + \% \text{ of H})$$

For hydrocarbon:

If C_xH_y represents general formula of hydrocarbon, then its balanced equation of combustion becomes: $C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

Derivation of the equation:

Let a, b and c be unknown stoichiometric coefficient for O_2 , CO_2 and H_2O respectively.

Then $C_xH_y + aO_2 \rightarrow bCO_2 + cH_2O$

From which: $x = b$; $y = 2c$ or $c = \frac{y}{2}$ and $2a = 2b + c = x + \frac{y}{2}$ or $a = x + \frac{y}{4}$

Hence $C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

Example 2

Given that 0.54g of organic compound containing carbon, hydrogen and oxygen only yielded 1.03g of CO_2 and 0.64g of water on complete combustion.

- Calculate empirical formula of organic compound
- Given that vapour density of the compound is 23. Find the molecular formula.

Solution

In 44g of CO_2 there is 12g of C

- So in 1.03g of CO_2 there is $\frac{1.03}{44} \times 12$ g of C

Thus % by mass of C in the compound was $\frac{1.03 \times 12}{44 \times 0.54} \times 100\% = 52\%$

In 18g of H_2O there is 2g of H

- So in 0.64g of H_2O there is $\frac{2}{18} \times 0.64$ g of H

Thus % by mass of H is $\frac{2 \times 0.64}{18 \times 0.54} \times 100\% = 13.17\%$

Then % of O = $100 - (\% \text{ of H} + \% \text{ of C})$

Hence % of O = $100 - (13.17 + 52) = 34.83\%$

Constituent atoms	C	H	O
% composition of each	52	13.17	34.83
Mass of each in 100g of the compound	52g	13.17g	34.83g
Number of moles of each; $n = \frac{m}{M_r}$	$\frac{52g}{12g\text{mol}^{-1}}$ $= 4.33\text{mol}$	$\frac{13.17g}{1g\text{mol}^{-1}}$ $= 13.17\text{mol}$	$\frac{34.83g}{16g\text{mol}^{-1}}$ $= 2.15\text{mol}$
Divide by smallest to Get simpler ratio	$\frac{4.33\text{mol}}{2.18\text{mol}} = 2$	$\frac{13.17\text{mol}}{2.18\text{mol}} = 6$	$\frac{2.18\text{mol}}{2.18\text{mol}} = 1$

i) Hence empirical formula of the compound is $\text{C}_2\text{H}_6\text{O}$

$$M_r = \text{Vapour density} \times 2 = 23 \times 2 = 46$$

Let molecular formula of the compound be $(\text{C}_2\text{H}_6\text{O})_n$

$$\text{Then } 24n + 6n + 16n = 46; 46n = 46 \text{ or } n = 1$$

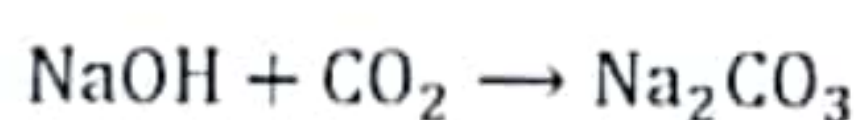
Hence molecular formula is $\text{C}_2\text{H}_6\text{O}$

Example 3

10cm^3 of hydrocarbon are exploded with excess oxygen. A contraction of 35cm^3 occurs all volumes being measured at room temperature and pressure. After treatment of the products with NaOH solution further contraction of 40cm^3 occurs, deduce molecular formula of hydrocarbon.

Solution

- Reagents present at the end of chemical reaction are water in liquid state, carbondioxide gas and unreacted oxygen gas (oxygen was in excess).
- Introduction of NaOH (or any other strong alkaline solution like KOH) absorbs CO_2 formed yielding carbonate as per equation;



- So further contraction of 40cm^3 is the volume of CO_2 which was absorbed after introduction of NaOH. Thus volume of CO_2 formed in the combustion was 40cm^3 .
- According to equation for the reaction which is $\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right)\text{O}_2 \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O}$
- It is clearly understood that volume of CO_2 is x times that of hydrocarbon (for gases volume ratio = mole ratio)
- Thus $10x = 40$ or $x = 4$
- Also before the introduction of NaOH: Final volume = Initial volume - 35

Let u be volume of unreacted oxygen in cm^3

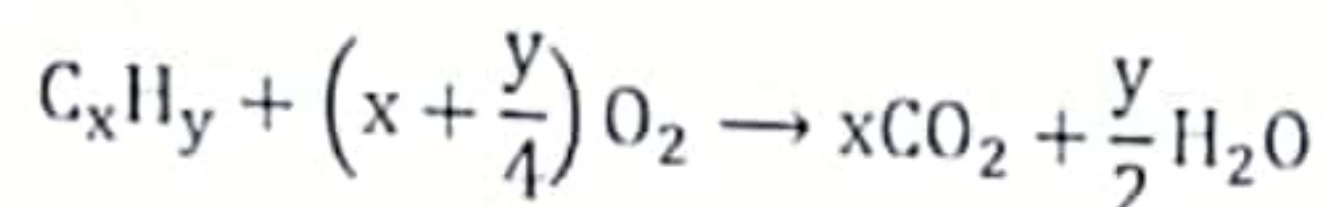
$$\text{Then } 40 + u = 10 + 10\left(x + \frac{y}{4}\right) + u - 35; 6.5 = x + \frac{y}{4}$$

Substituting $x = 4$ gives $2.5 = y/4$ or $y = 10$

Hence the molecular formula of hydrocarbon is C_4H_{10}

Example 4

20cm³ of gaseous hydrocarbon C_xH_y were exploded with 200cm³ of oxygen produce 140cm³ of gaseous products which contracted to 40cm³ after absorption with concentrated alkali all volumes were measured at temperature of 298K and pressure of 1atm. Find the values of x and y.

Solution

Volume of CO₂ was (140 - 40)cm³ = 100cm³

Volume of CO₂ is x times that of hydrocarbon C_xH_y

Then 20x = 100; x = 5

Volume of unreacted oxygen was (140 - 100)cm³ = 40cm³

Thus volume of reacted oxygen was (200 - 40)cm³ = 160cm³

So $20\left(x + \frac{y}{4}\right) = 160$; $x + \frac{y}{4} = 8$; but x = 5, thus $y/4 = 3$ or y = 12

Hence x = 5 and y = 12

PRACTICE EXERCISE 8

Problem 1

10cm³ Of a gaseous hydrocarbon required 20cm³ of oxygen for complete combustion, 10cm³ of carbon dioxide was produced; calculate the molecular formula of the hydrocarbon. (Answer CH₄).

Problem 2

A 1.155g sample of butyric acid, an organic compound containing carbon, hydrogen, and oxygen is analyzed by combustion and 2.308g of CO₂ and 0.9446g of H₂O are produced. In a separate experiment the molar mass is found to be 88.11g/mol. Determine the empirical and molecular formula of butyric acid. (Answer: C₂H₄O , C₄H₈O₂)

Problem 3

A 0.3410g sample of a carbon-hydrogen-oxygen was combusted to produce 0.75g of CO₂ and 0.1363g of H₂O . The molecular mass was determined to be 180amu. Determine the empirical and molecular formula of the compound. (Answer: C₉H₈O₄ , C₉H₈O₄).

Problem 4

A 0.821g hydrocarbon sample was combusted to yield 1.866g CO₂ and 0.7639g H₂O. The molecular mass was determined to be 116g/mol. Determine the empirical and molecular formulas of the compound (Answer : C₃H₆O , C₆H₁₂O₂)

Problem 5

A 0.2417g sample of a compound composed of C , H, O, Cl only, is burned in oxygen yielding 0.4964g of CO₂ and 0.0864g of H₂O. A separate 0.1696g sample of the compound is fused with sodium metal, the product dissolved in water and the chloride quantitatively precipitated with AgNO₃ to yield 0.1891g of AgCl .What is the empirical formula of the compound. (Answer: C₆H₅O₂Cl).

PART TWO

ALIPHATIC HYDROCARBONS

Chapter 9 HYDROCARBONS

INTRODUCTION

Hydrocarbon is an organic compound which consists of carbon and hydrogen only.

- Hydrocarbons consist of the following classes of organic compounds:

- Alkanes
- Alkenes
- Alkynes
- Arenes (aromatic hydrocarbons)

Alkanes, alkenes and alkynes in combination, are classified as aliphatic hydrocarbon.

- Depending on their saturated nature, hydrocarbons can be classified into two categories, namely:
- Saturated hydrocarbons and
 - Unsaturated hydrocarbons.

Saturated hydrocarbons are hydrocarbons with carbon-carbon single bond ($C - C$) as functional group.

- They are saturated because each carbon in the compound has four single sigma covalent bonds through sp^3 hybridised orbitals and the compounds have maximum number of hydrogen atoms they may contain. **Alkanes** fall under this category of hydrocarbons.

Unsaturated hydrocarbons are hydrocarbons with carbon-carbon multiple bond ($C = C$ or $C \equiv C$) as functional group.

- Due to presence of carbon-carbon multiple bond, unsaturated hydrocarbons do not take maximum number of hydrogen atoms in their molecules and hence they are unsaturated. Under this category, there are **alkenes**, **alkynes** and **arenes**.

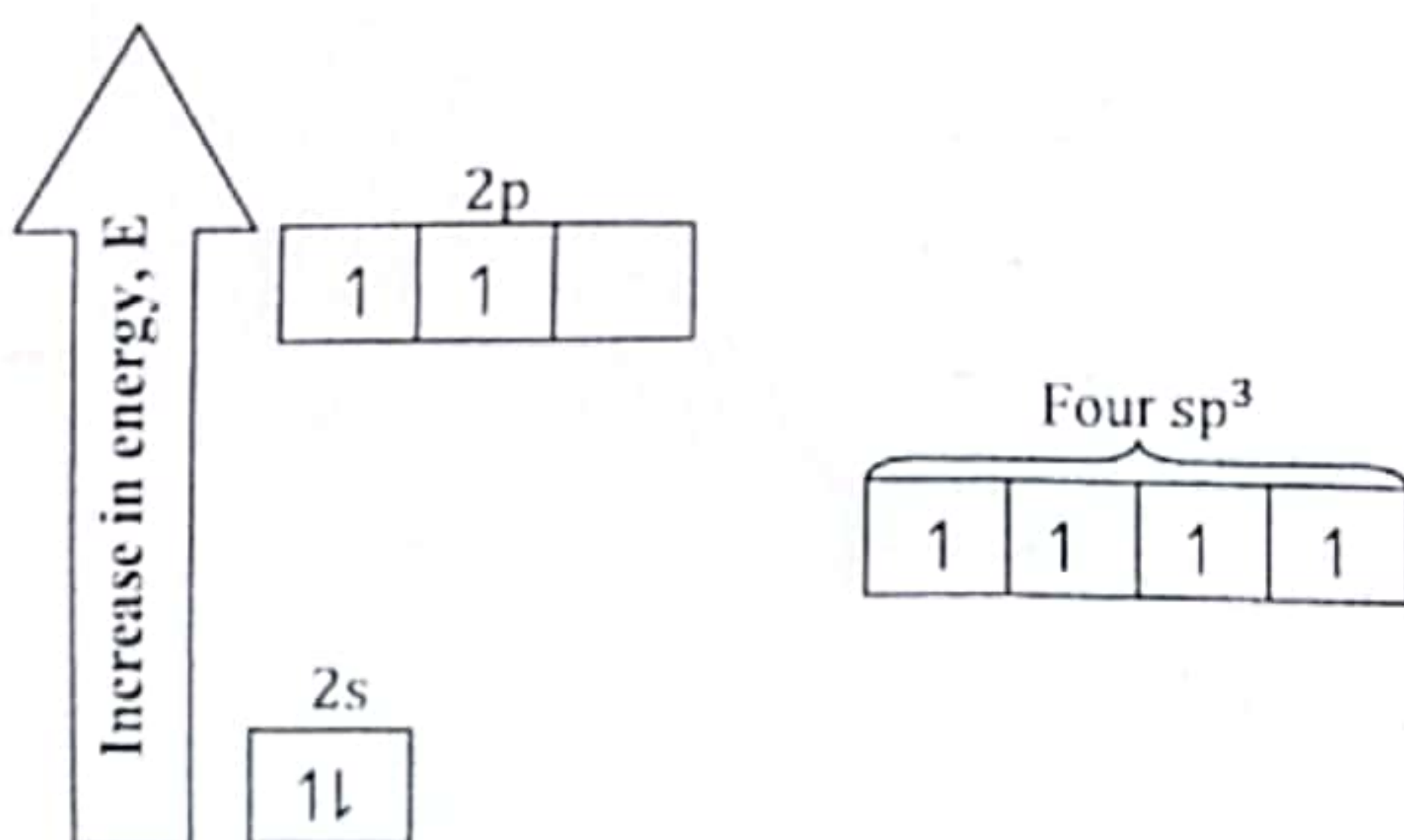
BONDING IN ALIPHATIC HYDROCARBONS

Aliphatic hydrocarbons may have carbon-carbon single bond ($C - C$) in alkane, carbon-carbon double bond ($C = C$) in alkene or carbon-carbon triple bond ($C \equiv C$) in alkyne.

Formation of carbon-carbon single bond in alkane

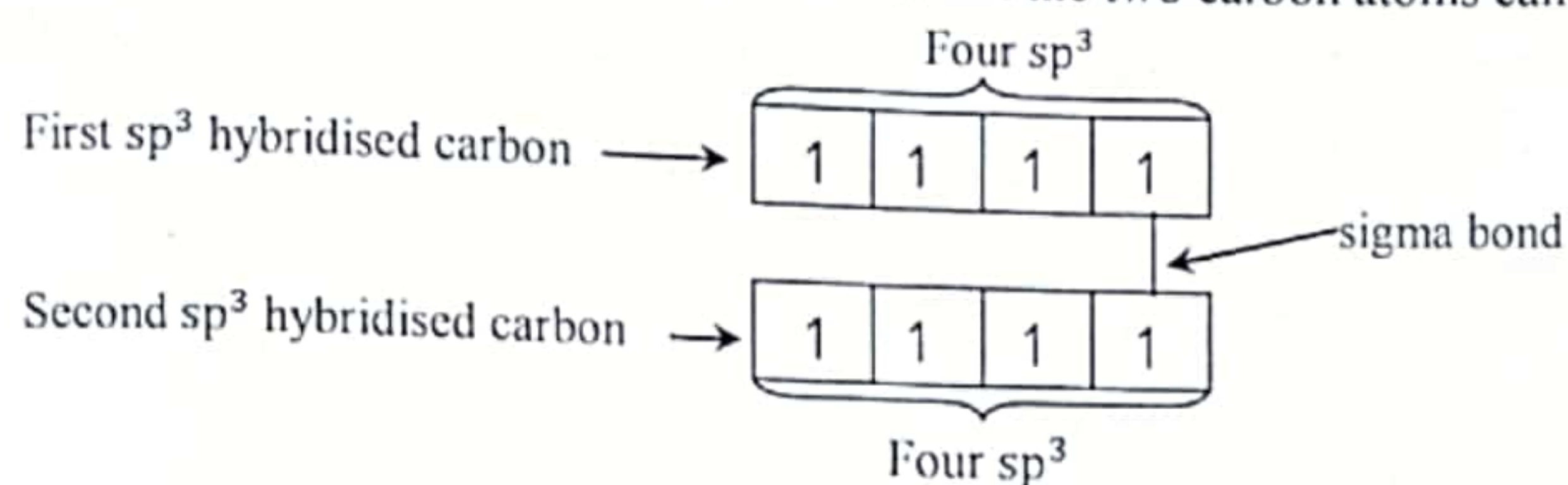
Presence of carbon-carbon single bond is explained by sp^3 hybridisation. To have better understanding of this, let us study bonding in ethane (CH_3CH_3).

- Consider sp^3 hybridisation in carbon illustrated below.

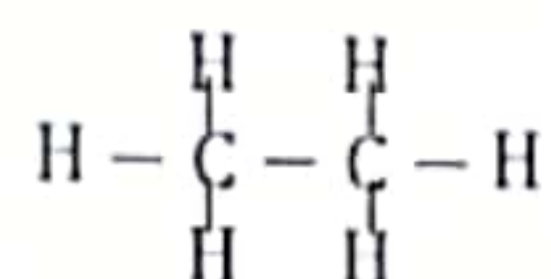


After hybridisation, sp^3 orbitals have equal energy which lies between that of 2s and 2p as illustrated in the above figure.

- If there is a second carbon which has undergone the same kind of hybridisation, the pair of sp^3 hybridised orbitals and the bond between the two carbon atoms can be illustrated as follows:



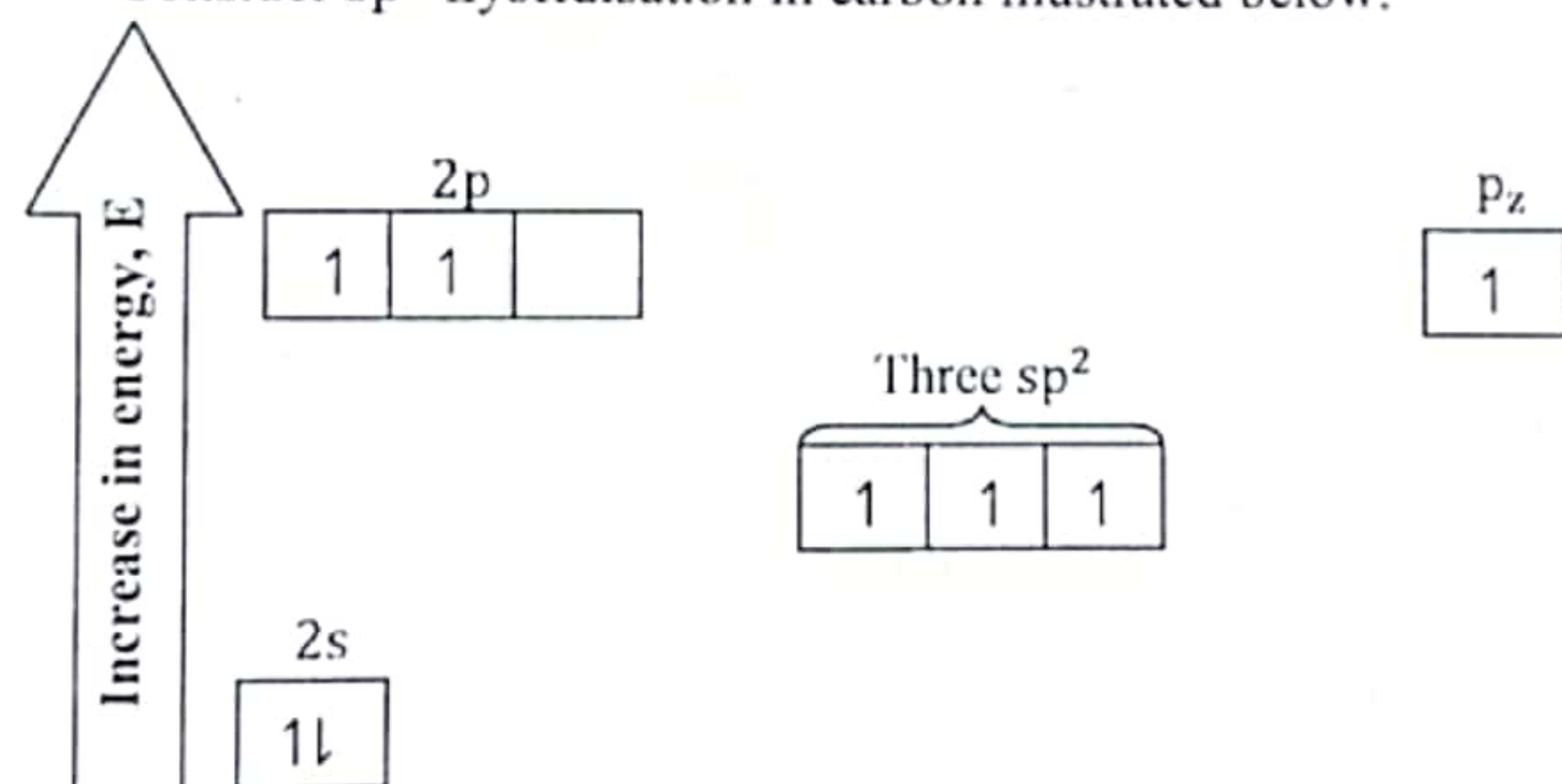
After formation of sigma bond between two hybridised orbital (one orbital from each carbon), each carbon becomes remained with three unpaired hybridised orbitals which are free to combine with other three monovalent atoms like hydrogen by sigma bond and hence the compound called ethane with the following structure is formed.



Formation of carbon-carbon double bond in alkene

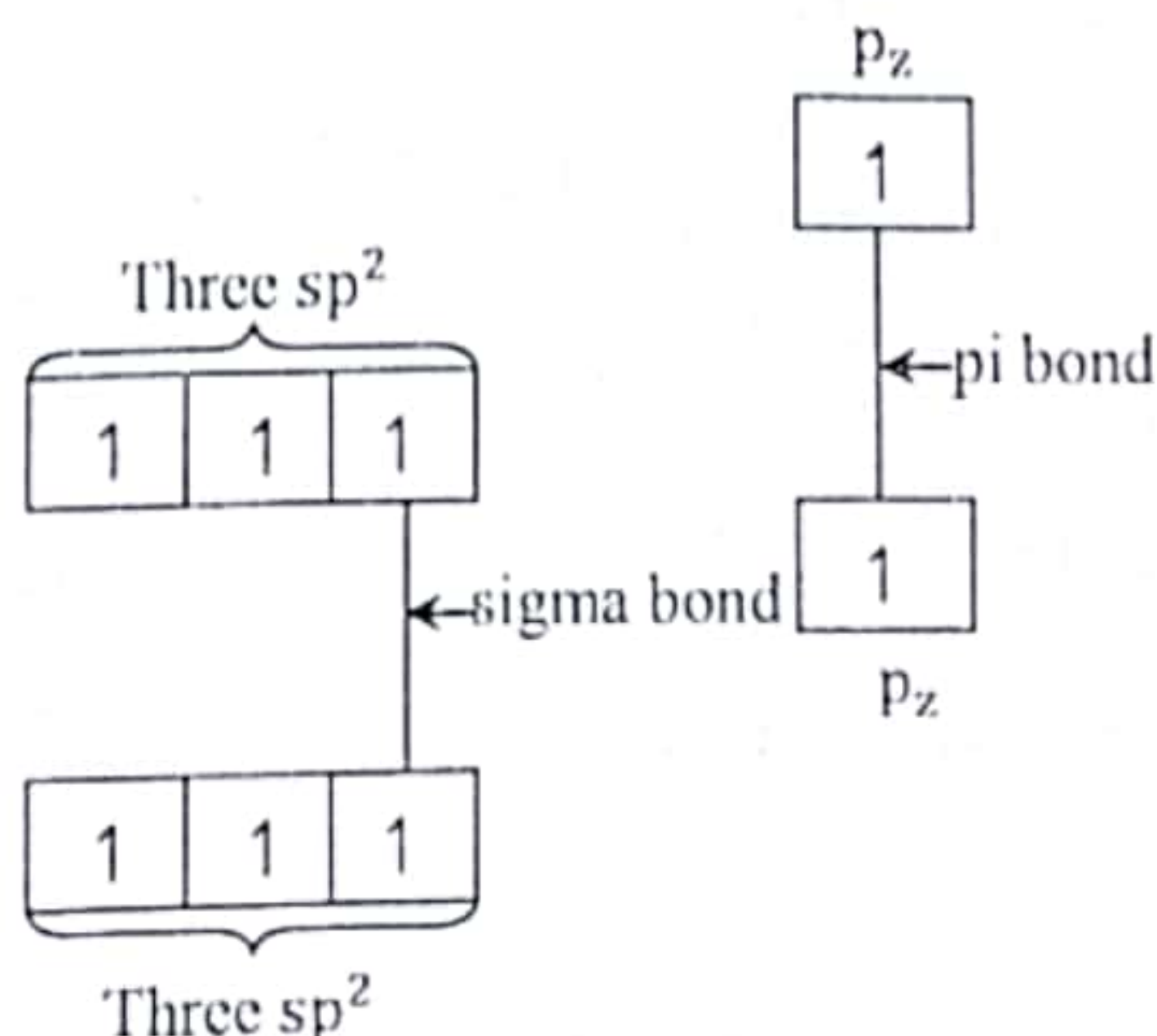
Presence of carbon-carbon double bond is explained by sp^2 hybridisation. To have better understanding of this, let us study bonding in ethene, $\text{CH}_2 = \text{CH}_2$.

- Consider sp^2 hybridisation in carbon illustrated below.



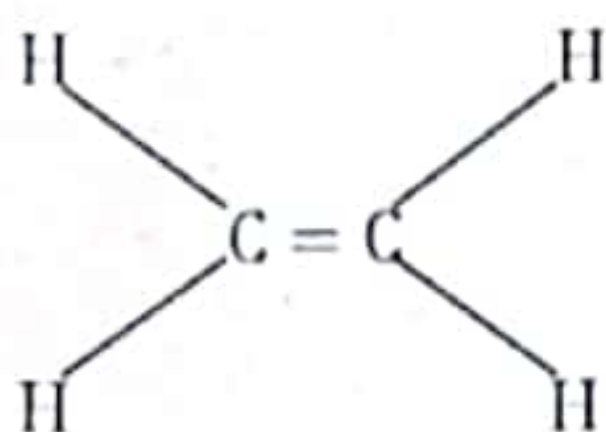
After hybridisation, sp^2 orbitals have equal energy which lies between that of 2s and 2p while one p orbital, p_z , remains unhybridised as illustrated in the above figure.

- If there is a second carbon which has undergone the same kind of hybridisation, the pair of sp^2 hybridised orbitals and the bond between the two carbon atoms can be illustrated as follows:



After formation of pi bond between two unhybridised p_z orbitals, sigma bond between hybridised sp^2 orbitals (one orbital from each carbon) must be formed too because pi bond is too weak to exist on its own without a help of sigma bond. This leads to the formation of carbon-carbon double bond.

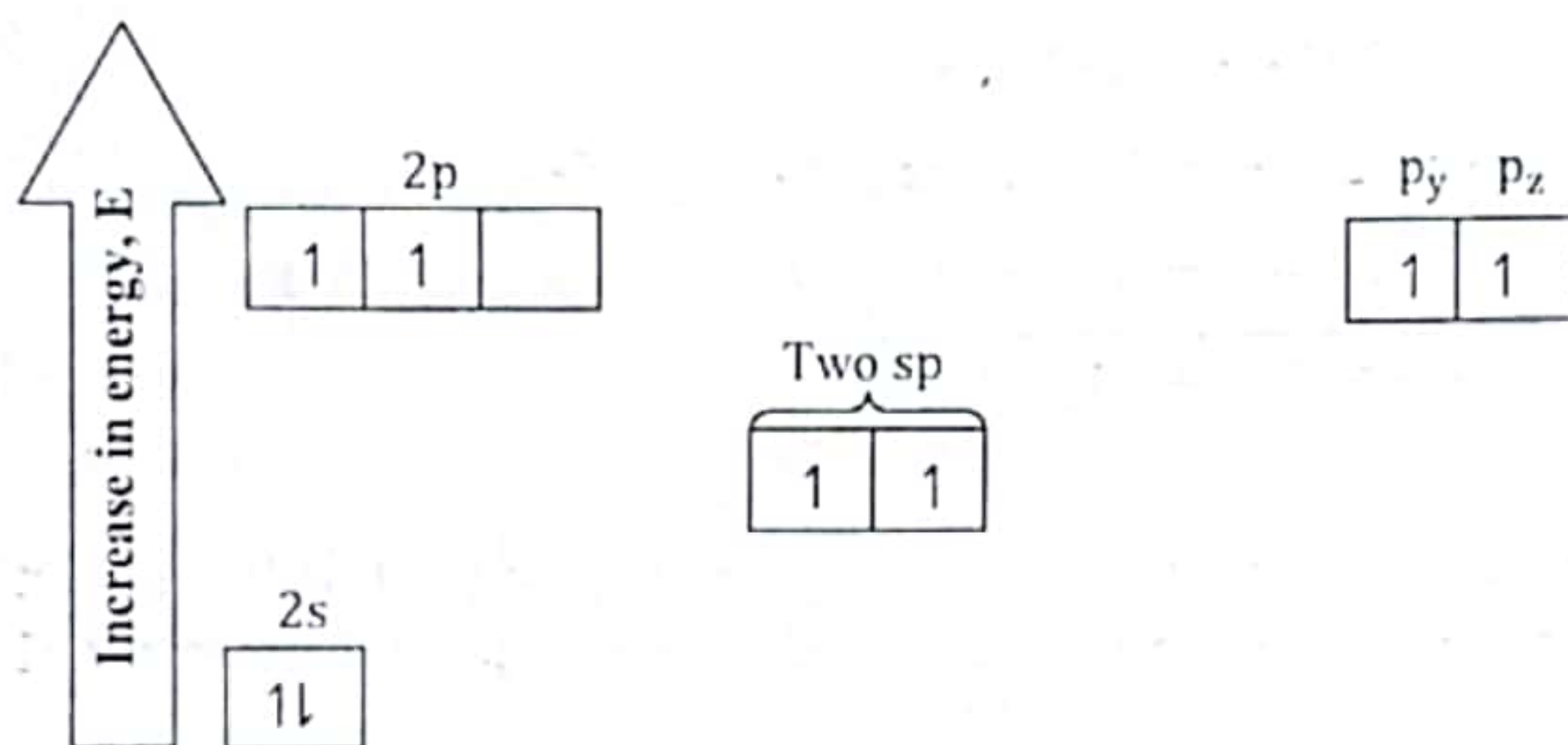
- Thereafter each carbon becomes remained with two unpaired hybridised orbitals which are free to combine with other two monovalent atoms like hydrogen by sigma bond and hence the compound called ethene with the following structure is formed.



Formation of carbon-carbon triple bond in alkyne

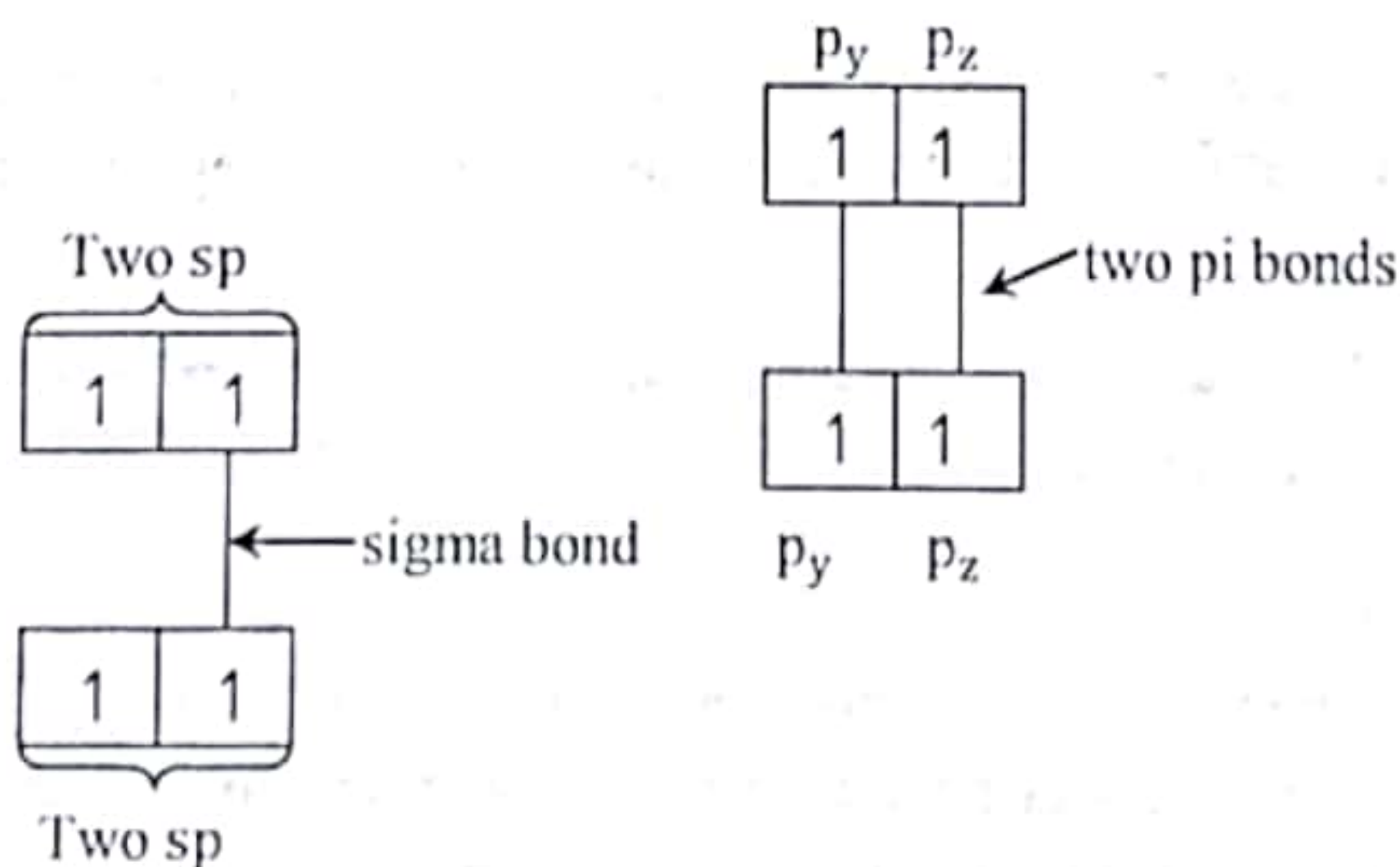
Presence of carbon-carbon triple bond is explained by sp hybridisation. To have better understanding of this, let us study bonding in ethyne, $\text{CH} \equiv \text{CH}$.

- Consider sp hybridisation in carbon illustrated below.



After hybridisation, sp orbitals have equal energy which lies between that of $2s$ and $2p$ while two p orbitals, p_y and p_z , remains unhybridised as illustrated in the above figure.

- If there is a second carbon which has undergone the same kind of hybridisation, the pair of sp hybridised orbitals and the bond between the two carbon atoms can be illustrated as follows:



After formation of pi bond between two pairs of unhybridised p_y and p_z orbitals, sigma bond between hybridised sp orbitals (one orbital from each carbon) must be formed too because pi bonds are too

weak to exist on their own without a help of sigma bond. This leads to the formation of carbon-carbon triple bond.

- Thereafter each carbon becomes remained with one unpaired hybridised orbitals which is free to combine with a monovalent atom like hydrogen by sigma bond and hence the compound called ethyne with the following structure is formed. $\text{H} - \text{C} \equiv \text{C} - \text{H}$

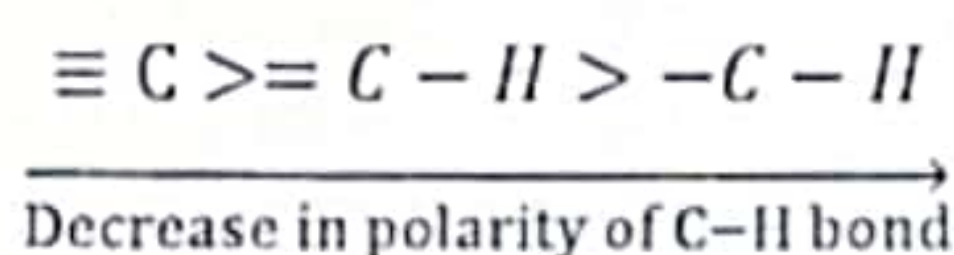
Very important to note that:

Being sp hybridised the percentage of s -characters in triple-bond carbon is 50% (one s -orbital out of total of 2 hybridised orbital, i.e. $1/2 \times 100 = 50\%$) which is largest for all kinds of carbon-carbon bond. sp^2 orbitals on double-bond carbon of alkene has 33% ($1/3 \times 100 = 33\%$) and sp^3 orbitals on single-bond carbon of alkane with 25% ($1/4 \times 100 = 25\%$) has smallest s -characters.

- This means electrons in sp orbitals of triple-bond carbon of alkyne are closer to the carbon nucleus than are electrons in sp^2 or sp^3 orbitals of double bond carbon or single bond carbon respectively.
- In an alkyne, the sp -hybridised carbon is therefore more electronegative than most other carbon atoms. Thus, an alkyne C-H bond is more polar than an alkene C-H bond or an alkane C-H bond.



Generally the polarity of bond in CH bond is accordance to the following order:



Don't be confused!

However generally $\text{C} - \text{H}$ are still non-polar compared to common strong polar bond we know. So it is always generalized that hydrocarbon are non-polars although there are some polar character of CH bond as explained above.

PHYSICAL PROPERTIES OF ALIPHATIC HYDROCARBONS

Molecules of aliphatic hydrocarbons are generally **non-polar covalents**. This provides the basis of explanation of their physical properties.

Solubility

Aliphatic hydrocarbons consist of non-polar molecules, so they tend to dissolve in non -polar solvents like organic solvents or other member of aliphatic hydrocarbons but they are insoluble in polar solvents like water.

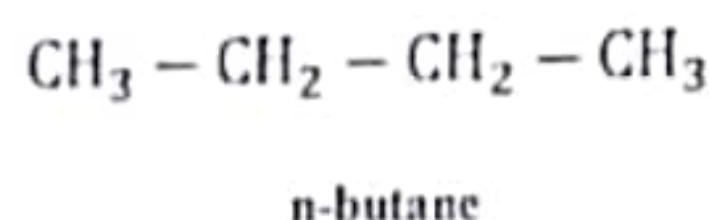
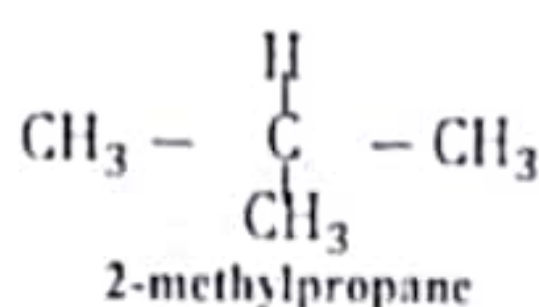
- However alkynes are slight soluble in water due to presence of sp hybridised carbon in $\text{C} \equiv \text{C}$ which make them slight polar.

Melting and boiling points

Aliphatic hydrocarbons are non-polar covalent bonded molecules, so their melting and boiling points are determined by strength of Van-der-waals force of attraction which inturn it (the Van-der-waals force of attraction) determined by molecular mass of the compound; i.e Van-der waals force of attraction increases with increase in molecular mass and vice-versa.

- In case of aliphatic hydrocarbons, molecular mass increases with an increase of number of carbon atoms (i.e. as length of carbon chain increases) and hence melting and boiling points of the hydrocarbons increase as number of carbons in the chain increases.
- For the same class of hydrocarbon with the same number of carbons (isomers), **hydrocarbon which is more branched (with greater number of branches) has lower boiling point** due to the following reasons:
 - Poor package of atoms in more branched chain
 - Smaller surface area in more branched hydrocarbon because it is more spherical in shape which has minimum surface area.

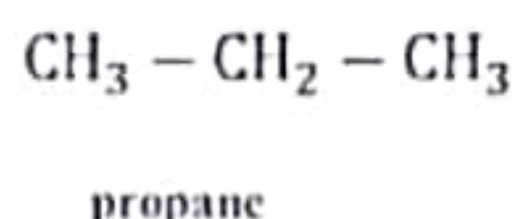
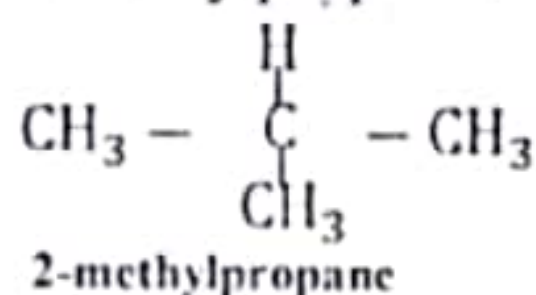
For example 2-methylpropane has lower boiling point than its corresponding straight chain isomer, n-butane.



Don't misunderstand!

Factor of number of carbon atoms and hence molecular weight has greater influence on strength of Van-der-waals force of attraction than the factor of number of branches.

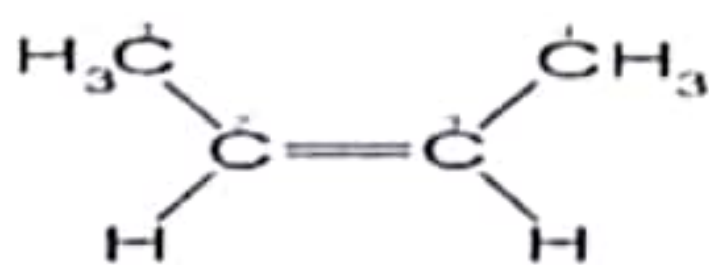
- A hydrocarbon with greater number of carbon atoms has greater boiling point than hydrocarbon with fewer carbon atoms even if the hydrocarbon (with greater number carbons) is more branched. For example 2-methylpropane has greater boiling point than propane.



For geometric (cis-trans isomers) alkenes, **the trans isomer has lower melting and boiling point, why?**

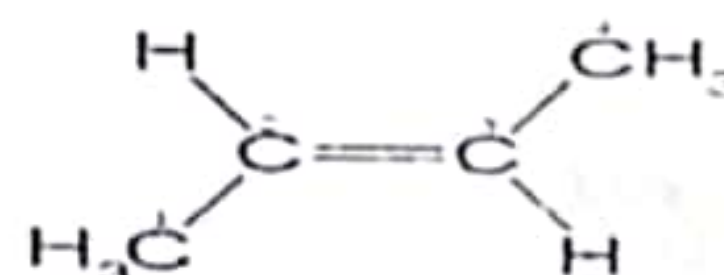
The sp^2 carbon in alkene is enough electron-withdrawing to create a weak dipole moment along the substituent attached to it. The two individual dipoles together form a net molecular dipole.

- In trans-substituted alkenes, the dipole moment cancels each other out because the substituents are in opposite side thus making it purely non-polar.
- In cis-substituted alkenes there is a net dipole moment making it polar the fact which contributes to higher melting and boiling points in cis-isomers than trans-isomers. For example cis-but-ene has higher boiling point than trans-but-ene for this reason.



Cis-but-2-ene

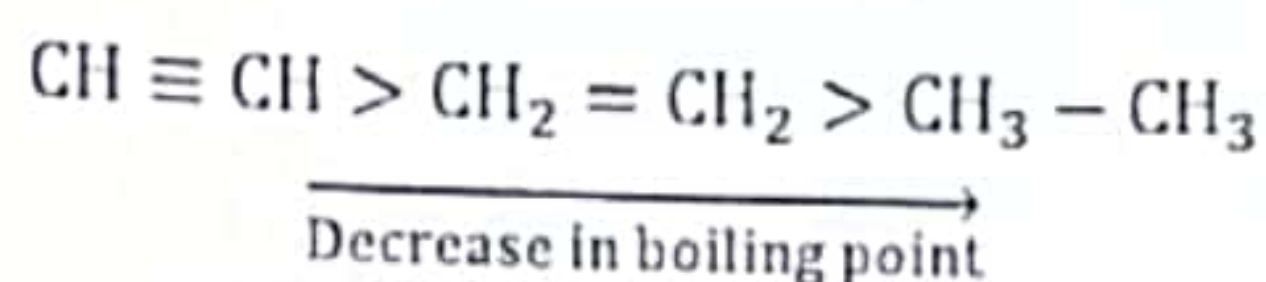
(There is non-zero net dipole moment)



Trans-but-2-ene

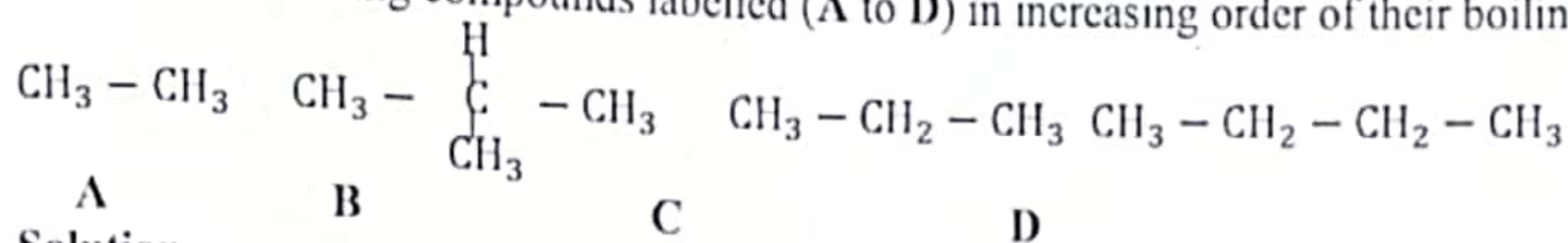
(There is zero net dipole moment)

- With three classes of hydrocarbons of equal number of carbon atoms, alkyne has highest melting and boiling point because it is most polar due to presence of the sp -hybridised carbon, followed by alkene which has sp^2 hybridised carbon and the last is alkane which has weakest electron-withdrawing sp^3 hybridised carbon with smallest s-characters. For example, boiling points of ethane, ethene and ethyne follow the following trend:

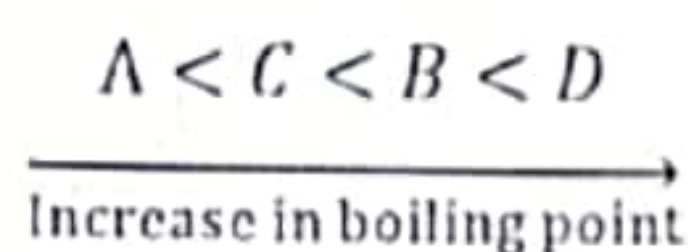


Example

Arrange the following compounds labelled (A to D) in increasing order of their boiling point.



Solution



Physical state

Lower members of aliphatic hydrocarbons are gases; are followed by members which are liquids and the higher members are solids at room temperature.

- This is because melting and boiling point of hydrocarbons increases as number of carbons (length of carbon chain) increases due to an increase in molecular weight and hence the increase in Van-der-waals force of attraction in the same trend.

Density

Density of aliphatic hydrocarbons increases with an increase of number of carbons (i.e as length of carbon chain increases) due to increase of their molecular masses in the same trend.

PRACTICE EXERCISE 9

Problem 1

What type of hybridisation of each carbon of $\text{CH}_3\text{CH}=\text{CH}_2$

Problem 2

What is the percentage of s and p characters of:

- A carbon in CH_4
- Second carbon in $\text{CH}_3\text{CH}=\text{CHCH}_3$
- First carbon in $\text{CH}_3\text{C}\equiv\text{CH}$

Problem 3

Arrange the following compounds in order of increasing their acidic characters, giving reasons for your arrangement $\text{CH}_2=\text{CH}_2$, CH_3CH_3 , $\text{CH}_2=\text{CH}_2$

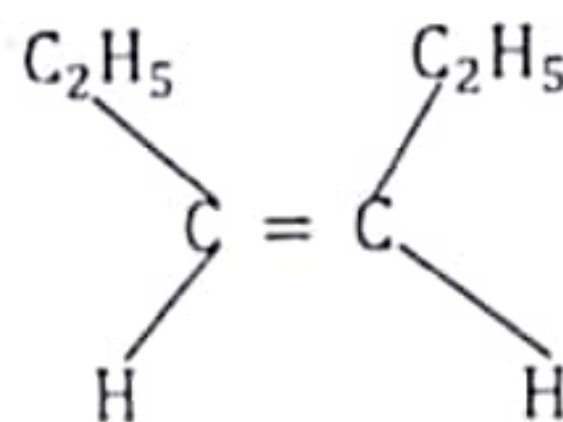
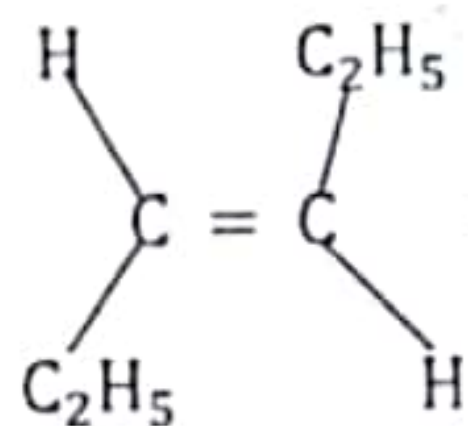
Problem 4

Although CH_3CHCH_3 , has the same molecular weight as $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 CH_3

boiling point of the former is lower than that of the later. Explain

Problem 5

Compare boiling point of the following compounds:



Chapter 10 ALKANES

INTRODUCTION

Alkanes are saturated hydrocarbons with carbon-carbon single bond as functional group.

- Saturated nature of alkanes make them to be less reactive, that is why are known as paraffins (it derived from two latin words 'parum' means 'little or lack' and 'affinis' means reactivity).

Alkanes (excluding cyclic alkanes) have general molecular formula of C_nH_{2n+2} .

The first ten members of alkane are listed in the table below

ALKANES	NAME
CH_4	methane
C_2H_6	ethane
C_3H_8	propane
C_4H_{10}	butane
C_5H_{12}	pentane
C_6H_{14}	hexane
C_7H_{16}	heptane
C_8H_{18}	octane
C_9H_{20}	nonane
$C_{10}H_{22}$	decane

ALKYL GROUPS

Alkyl groups are molecules of hydrocarbons which are formed after removing one hydrogen atom from alkanes.

- They are also known as **alkyl radicals** or simply **radicals** and hence they commonly abbreviated by letter **R**.
- Aliphatic alkyl groups have general molecular formula of C_nH_{2n+1}

Unbranched alkyl group are simply named after its own alkane parent with the **-ane** ending replaced by **-yl**; for example CH_4 is **methane**, therefore the CH_3- group is **methyl** group.

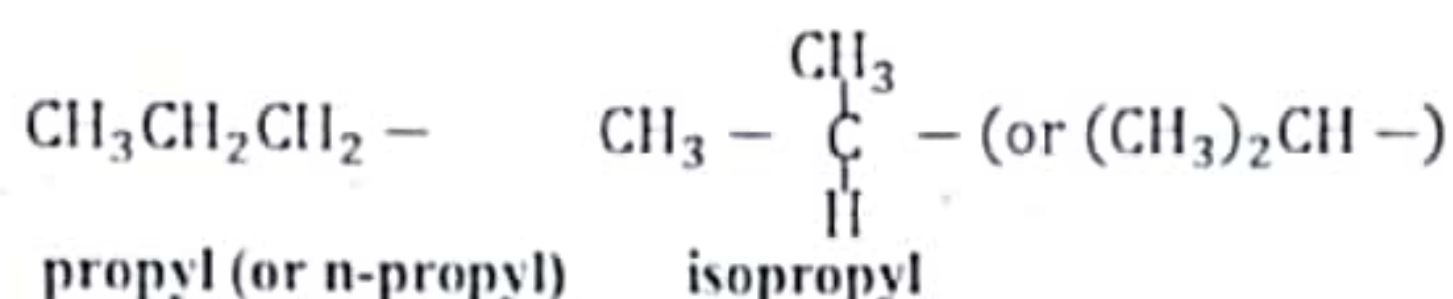
The first four unbranched alkyl groups

ALKANES	MOLECULAR FORMULA OF ALKYL GROUPS	STRUCTURE OF ALKYL GROUPS	IUPAC NAME
CH_4	$\text{CH}_3 -$	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \\ \quad \\ \text{H} \quad \text{H} \end{array}$	methyl
$\text{CH}_3\text{CH}_3 (\text{C}_2\text{H}_6)$	$\text{C}_2\text{H}_5 -$	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \\ \quad \\ \text{H} \quad \text{H} \end{array}$	ethyl
$\text{CH}_3\text{CH}_2\text{CH}_3 (\text{C}_3\text{H}_8)$	$\text{C}_3\text{H}_7 -$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	propyl
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (C_4H_{10})	$\text{C}_4\text{H}_9 -$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	butyl

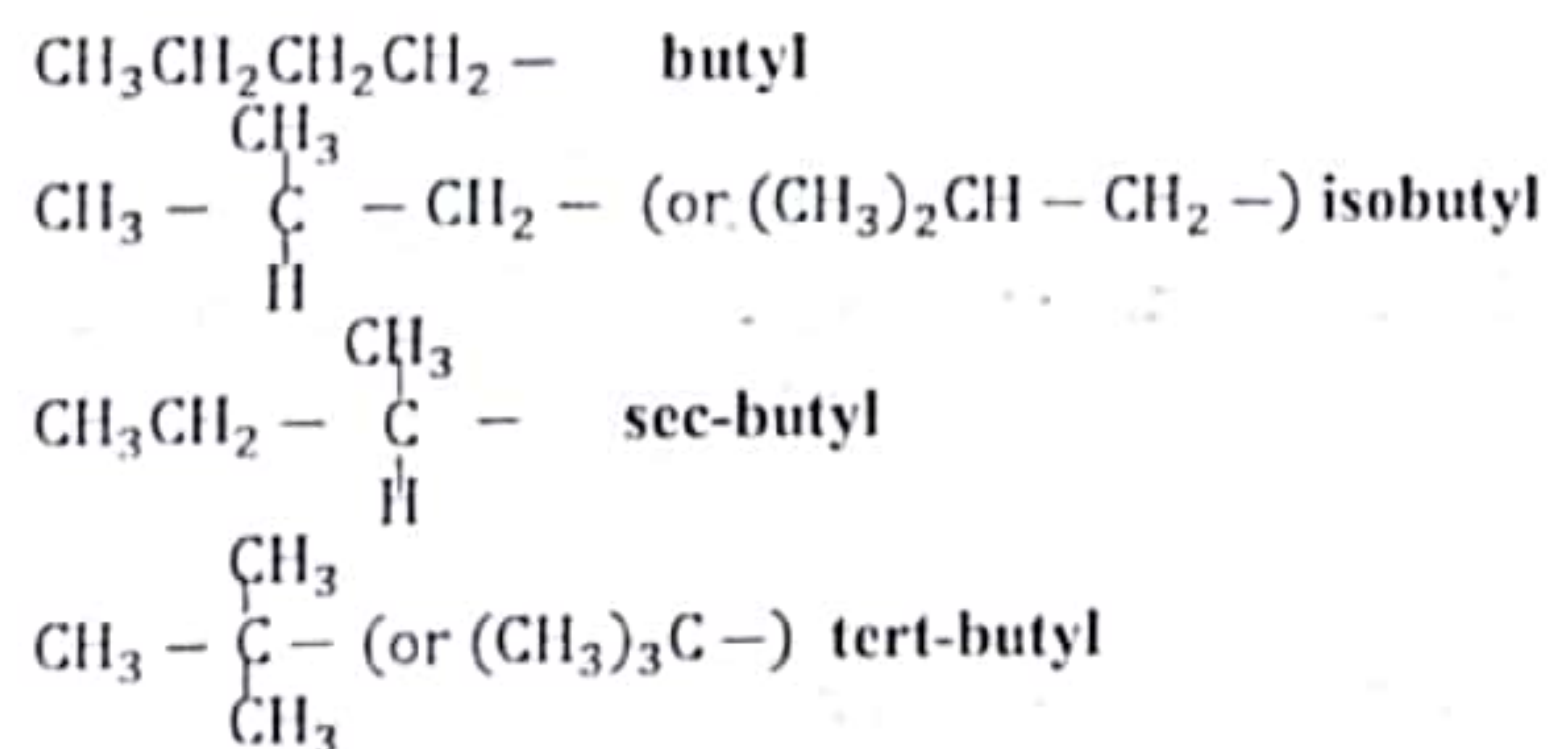
Branched alkyl groups

An alkyl group may be branched, rather than a straight chain.

- Common branched alkyl groups have **common** (or **trivial**) names. For example, the alkyl group with three carbons ($\text{C}_3\text{H}_7 -$) have the following two possible isomers:



- The use of prefix n- (for normal) emphasizes that the chain is straight. Its use is unnecessary since the absence of any prefix indicates a carbon chain is straight (unbranched).
- The prefix **iso-** (for isomeric-) is used to show that the continuous carbon chain terminates on $(\text{CH}_3)_2\text{CH} -$ group.
- Other important structural prefix for branched alkyl group with more than three carbons are:
 - **sec-** (for secondary-) indicates that the attaching (head) carbon is secondary (a carbon bonded to two carbons).
 - **tert-** or **t-** (for tertiary) indicates that the attaching carbon is tertiary (a carbon bonded to three carbons).
- For example, a four-carbon alkyl has the following structural isomers:



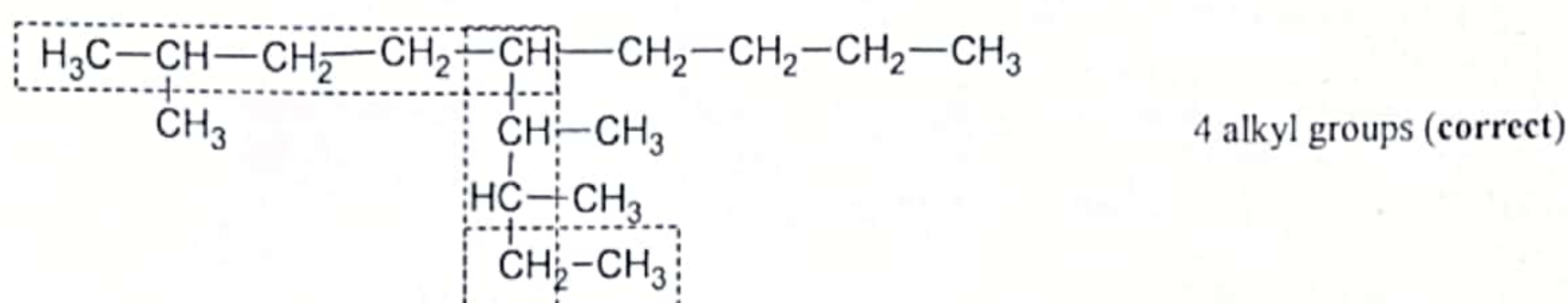
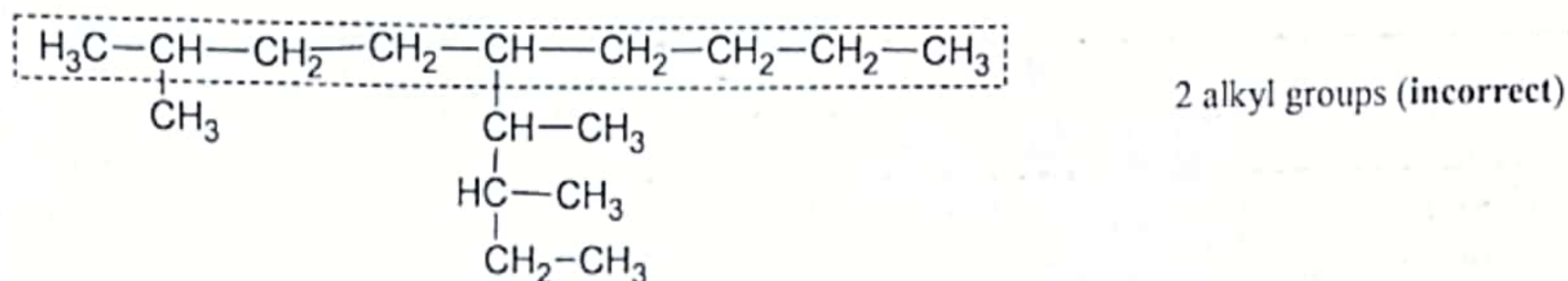
SYSTEMATIC NOMENCLATURE OF ALKANES

International union of pure and applied chemistry (IUPAC) established rules for systematic nomenclature of organic compounds although sometime common names are still used for convenience and historical development.

- The following hints from IUPAC are very useful in nomenclature of alkanes. These hints provide the basis of naming any other organic compound.

Recognition of parent chain

- The longest continuous carbon chain is the parent chain.
- If there is more than one longest continuous carbon chain, then the carbon chain which is more branched (with greater number of attached groups) becomes the parent chain. To insist....! In this case you have alternative parent chain but you have no alternative parent chain!



Warning!

In determining parent chain, most students make a mistake of looking in the horizontal chain only. Be careful, don't fall in that trap!

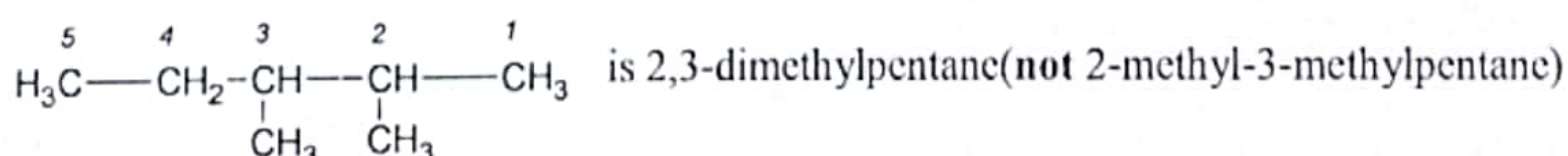
Numbering of carbon atoms in the parent chain

Lowest sum rule is all about numbering of carbon chain. It states that: *Numbering of carbon atoms in the parent chain should be done in such a way that numbers representing position of substituents (attached groups) must have lowest sum.*

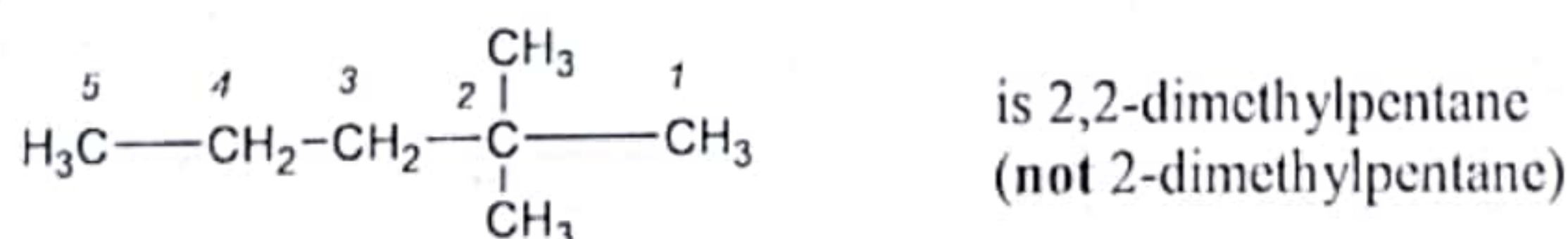
- In other words, numbers showing position of attached groups should be as small as possible. If there is only one attached group, numbering should simply start at the end closer to the group.
- If start numbering from either direction gives the same effect on the summation, then priority goes to the group which starts to be named according to alphabetical order; i.e numbering should start at the end which is closer to the group which starts to be named alphabetically.

Dealing with attached (substituent) groups

- Position of substituent (attached) group should be shown by using Arabic numerals.
- If there is more than one substituent (attached) group of the same type, use the following prefixes to represent number of attached groups of the same type present: di for two, tri for three, tetra for four, penta for five, etc.



- If the same type of substituents is attached at the same carbon, the number representing position of the substituents should be repeated at equal times as it appears at the carbon.



- Naming of substituents should follow alphabetical order regardless to their positions (number they take), numerical prefixes they carry and their complexity; e.g 3,3,4-triethyl is named before 2-methyl.
- Numbers representing position of substituents are separated by using commas (,) but number and word are separated by using hyphen (-).

Be careful!

Numerical prefixes like di, tri, and tetra are not alphabetized because have nothing to do with the structure of alkyl groups. However structural prefixes like iso, sec and tert are alphabetized. For example trimethyl (here **m** is alphabetized, tri just represents number of methyl groups in the compound) is named before propyl while isopropyl (here **i** from iso is alphabetized because the prefix iso gives the information about the structure of the alkyl group) is named before methyl.

Naming the compound

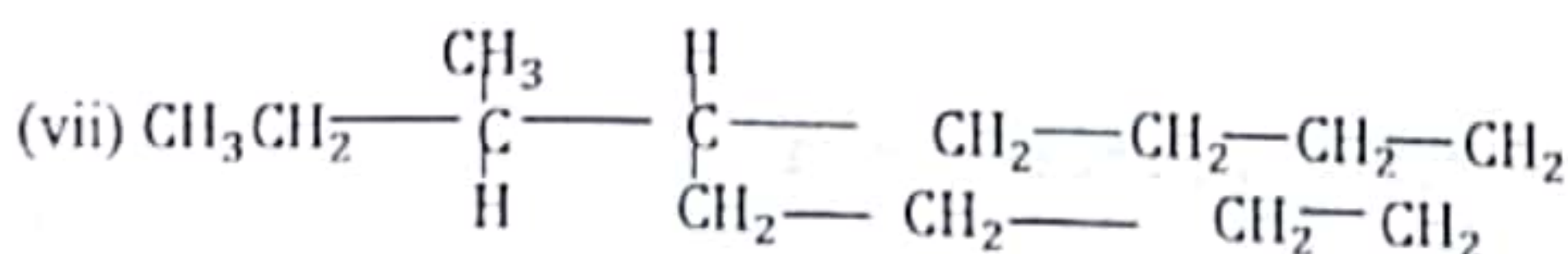
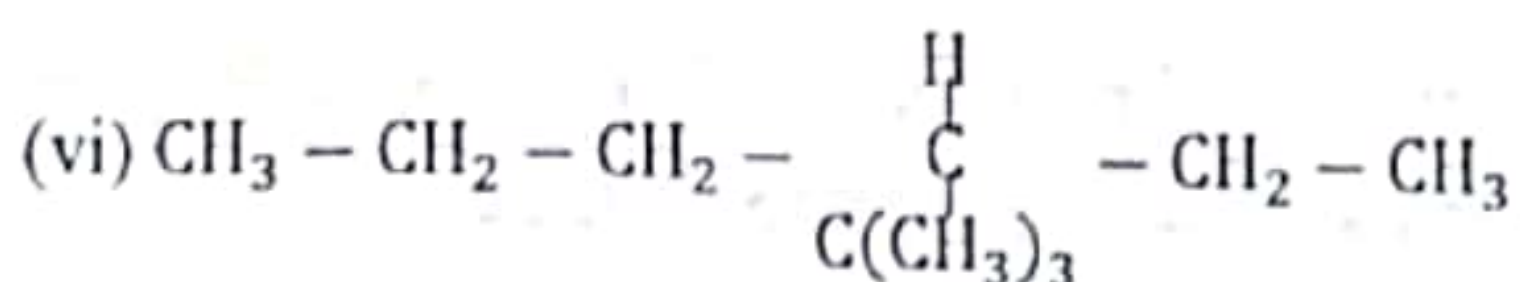
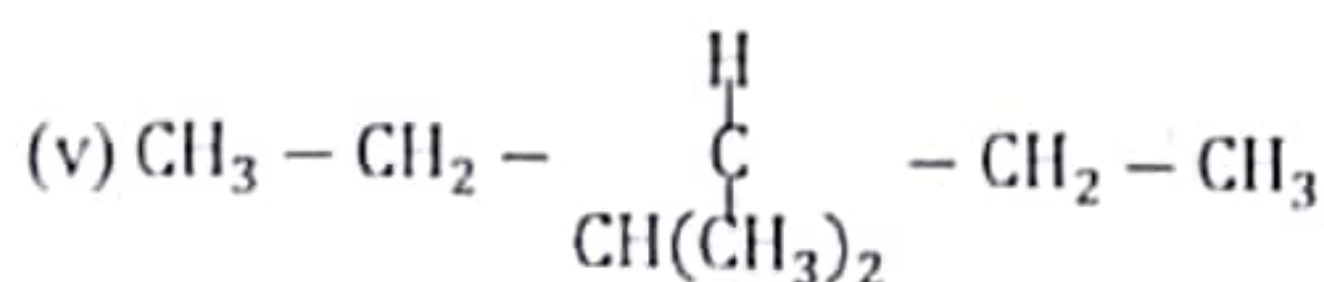
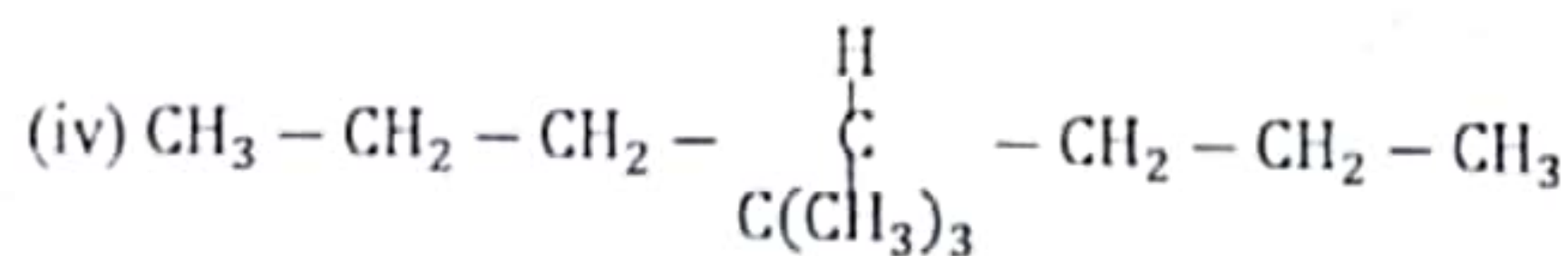
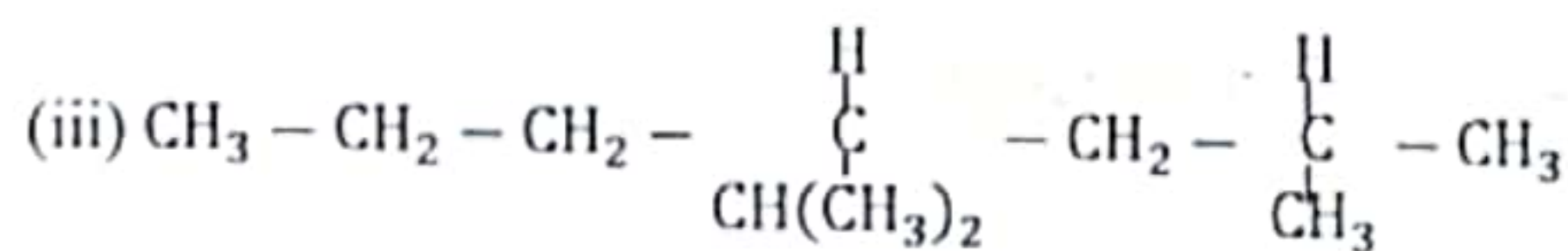
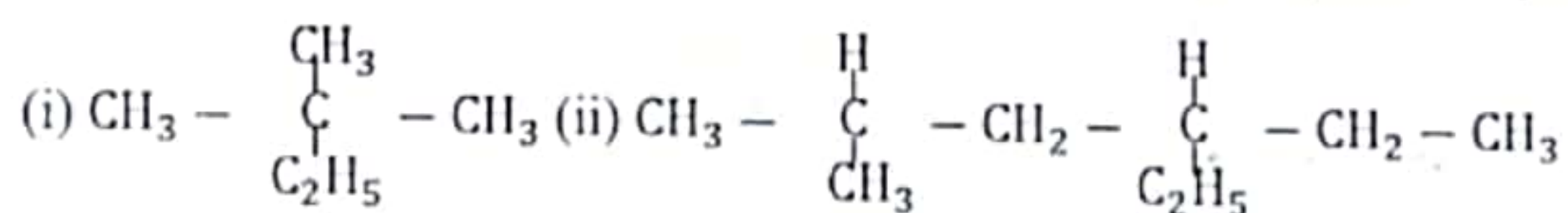
In naming alkanes, attached groups are named first followed by parent name and the parent name must end with suffix -ane.

Warning!

Most students do a mistake of leaving a little space between name(s) of attached groups and parent name, e.g. 2-methyl pentane; this is **incorrect**. The **name of organic compound must be written as a single word**. Therefore instead of writing 2-methyl pentane, the **correct** way of writing the name is to write 2-methylpentane.

Example 1

Give the systematic (IUPAC) names of the following organic compounds.



Solution

(i) **2,2-dimethylbutane** (Incorrect recognition of parent chain by looking at horizontal chain only, leads to the **incorrect** name which is 2-ethyl-2-methylpropane. So you should take care of that)

(ii) **4-ethyl-2-methylhexane** (Attached groups are named according to their alphabetical order regardless to their position)

(iii) **4-isopropyl-2-methylheptane** (Here there is 'i' from structural prefix 'iso' of 'isopropyl', which is lower alphabet than 'm' of methyl so isopropyl is written before methyl although 'propyl' or even with numerical prefixes of alphabet than 'm' of 'methyl' like diethyl must be written after methyl).

(iv) **4-tert-butylheptane**

(v) **3-ethyl-2-methylpentane** (Don't take horizontal chain although it has five carbons. This is because with only one attached group, i.e. isopropyl group, the chain is less branched. **Remember**, if there is alternative longest continuous carbon chain, the chain with greater number of branches is what become the parent chain)

(vi) **3-ethyl-2,2-dimethylhexane** (Again there is alternative longest carbon chain! So the chain which is more branched is the parent chain)

(vii) **5-sec-butylnonane**

LINE FORMULA FOR STRUCTURAL FORMULA

A line formula for a structural formula is indicated by zig-zag lines. The point of meeting two lines indicates a $-\text{CH}_2$ group and the end of lines indicates a $-\text{CH}_3$ group.

For example, a line formula for CH_3CH_3 is 

Other examples are:

 for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (Or $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$)

 for $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (3 - methylpentane)

 for $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ (2,2 - dimethylbutane)

ISOMERISM IN ALKANES

Aliphatic alkane exhibits the following types of isomerism:

- Skeletal isomerism
- Position isomerism

Isomers of alkane are known as alkanes e.g isomers of butane with molecular formula of C_4H_{10} are known as butanes, isomers of pentane with molecular formula of C_5H_{12} are known as pentanes.

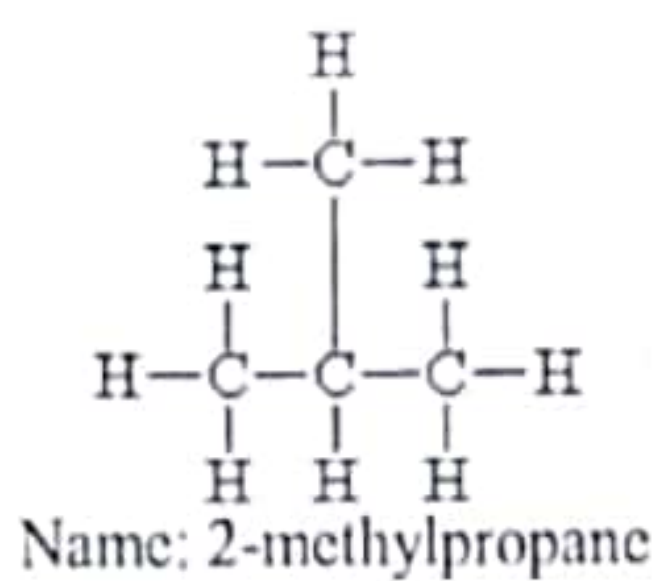
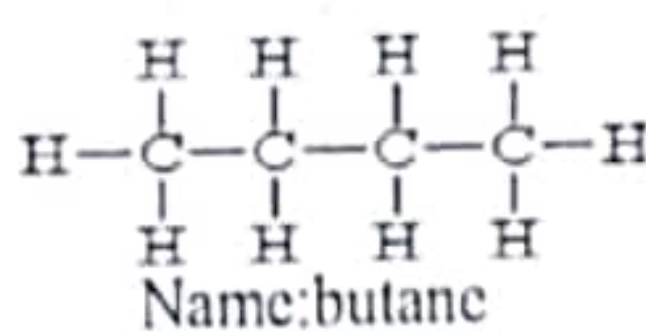
Example 2

Name all possible isomers of organic compounds with molecular formula

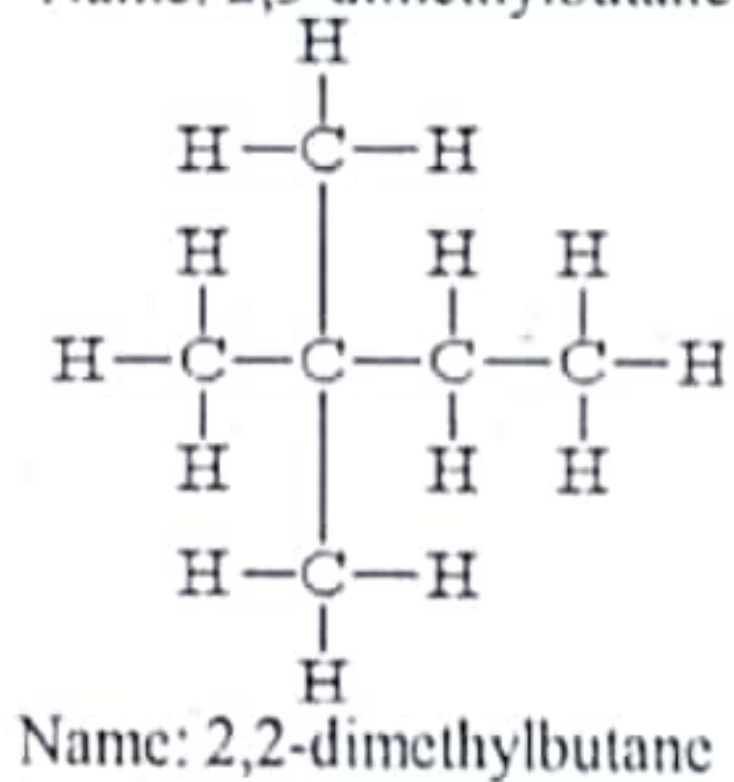
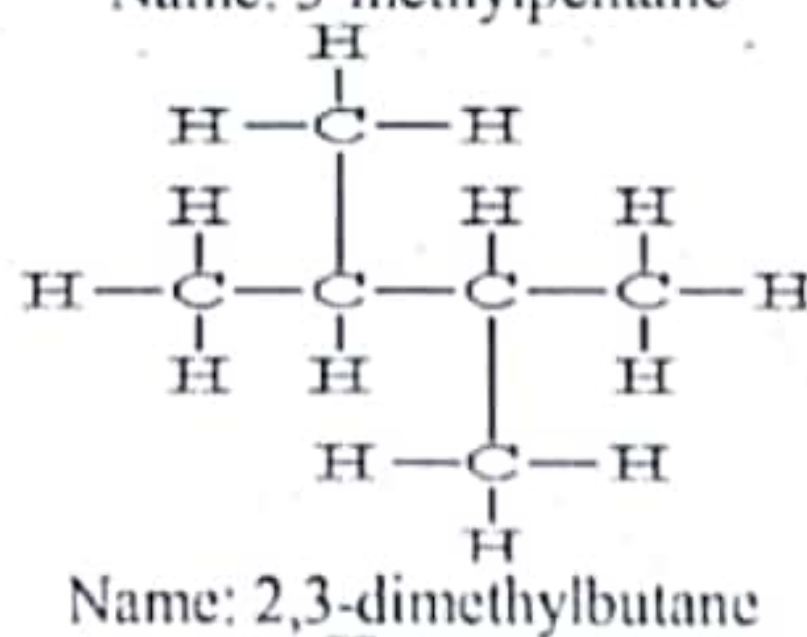
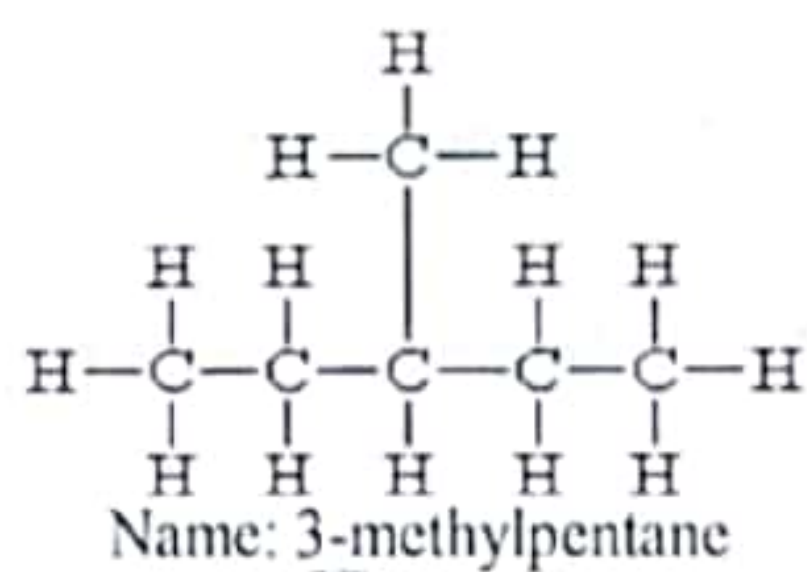
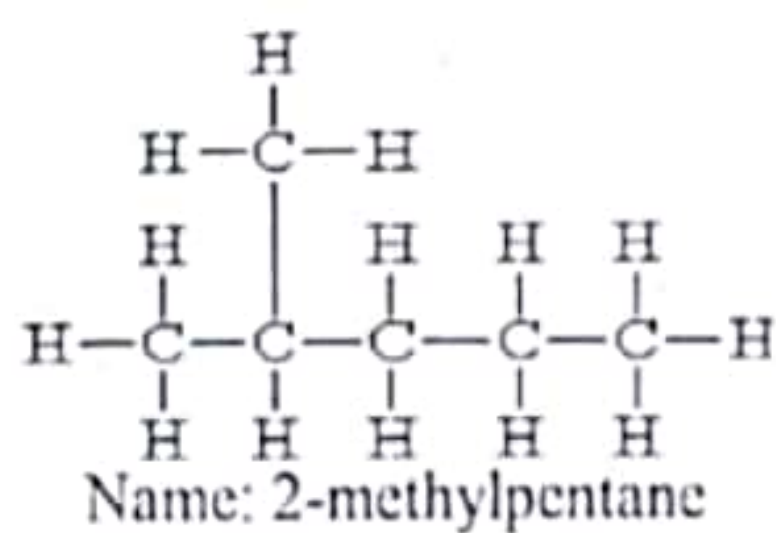
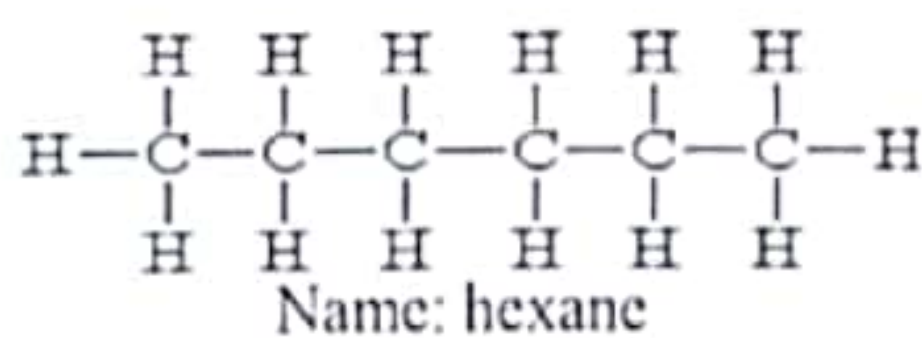
(i) C_4H_{10} (ii) C_6H_{12}

Solution

(i)



(ii)

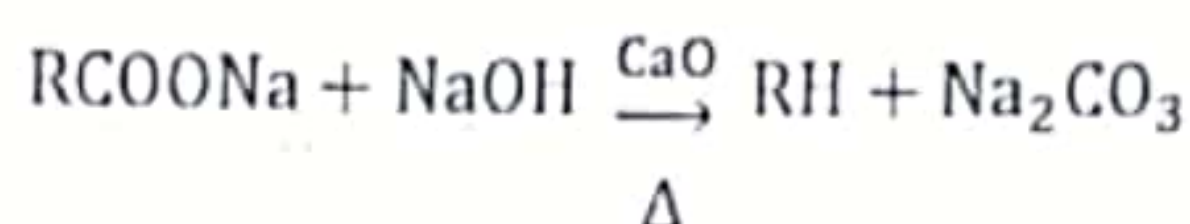


PREPARATIONS OF ALKANE

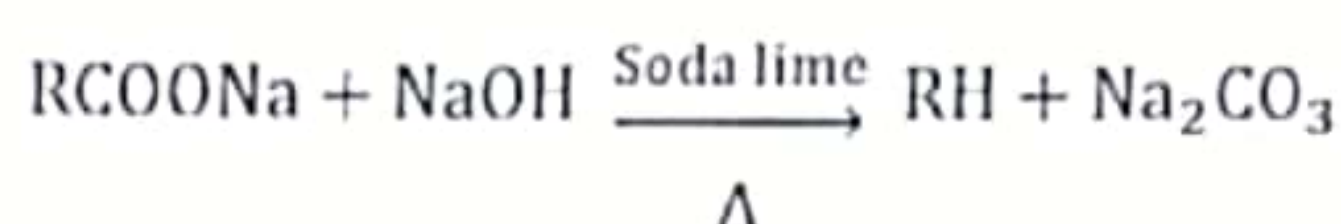
Decarboxylation of carboxylic salts

Decarboxylation means removal of CO_2 from molecules having carboxylic ($-\text{COO}$) group.

- When a carboxylic salt like sodium carboxylate is heated with the mixture of sodium hydroxide and calcium oxide, alkane is formed.



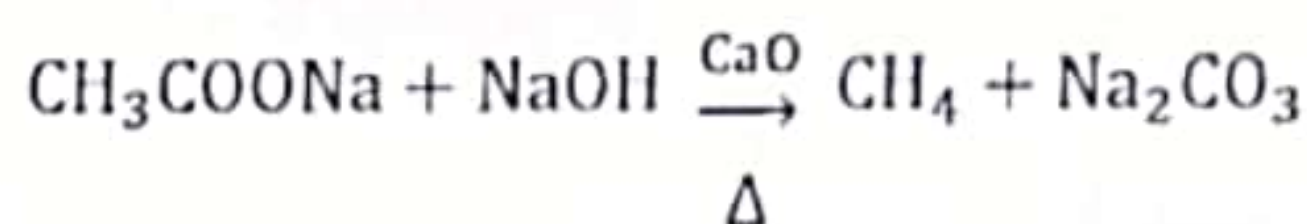
Mixture of NaOH and CaO is known as soda lime. So alternatively the equation must be written as follows:



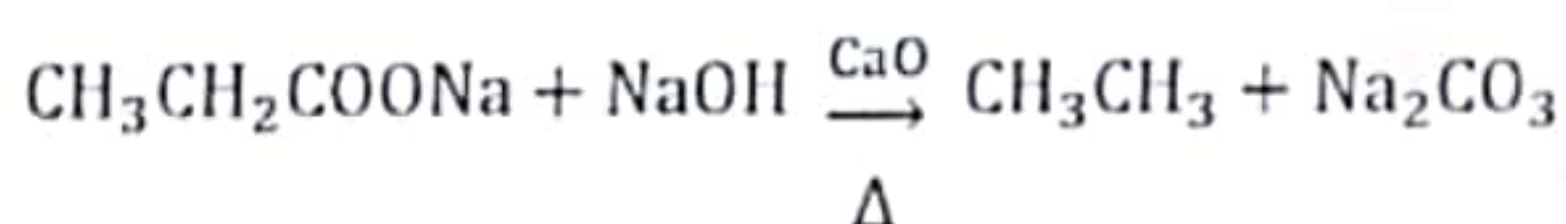
In the above reaction, CaO has the following significances:

- It makes the reaction milder than if NaOH (caustic soda) would be used alone thus enabling handling of materials. Otherwise the reaction will occur violently.
- Also CaO (CaO is good dehydrating agent) used alongwith NaOH keeps it dry (NaOH is hygroscopic) to aid fusion.

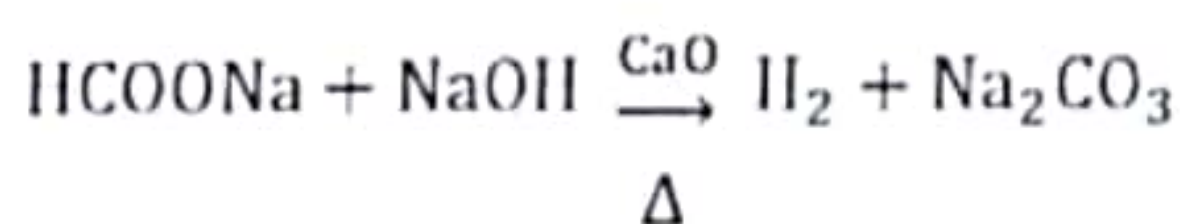
Example, heating sodium ethanoate with soda lime liberates methane gas.



Or heating of sodium propanoate with soda lime gives ethane gas.



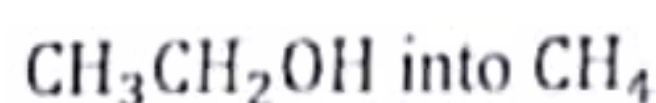
While heating of sodium methanoate with the soda lime liberates hydrogen gas.



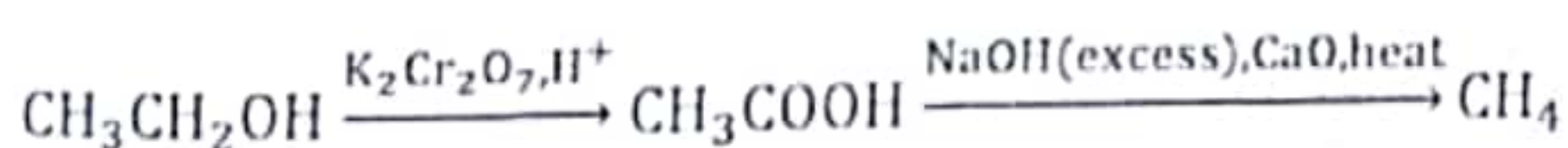
In the above reactions it clearly understood that number of carbons in the organic product is decreased by one, so the reaction is very important in dealing with conversion problems which show that number of carbons has decreased by one.

Example 3

Show how the following conversions may be achieved.



Solution

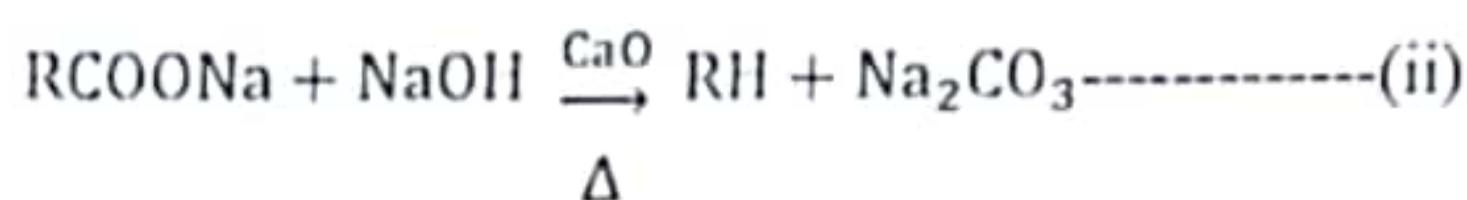


It should be noted that:

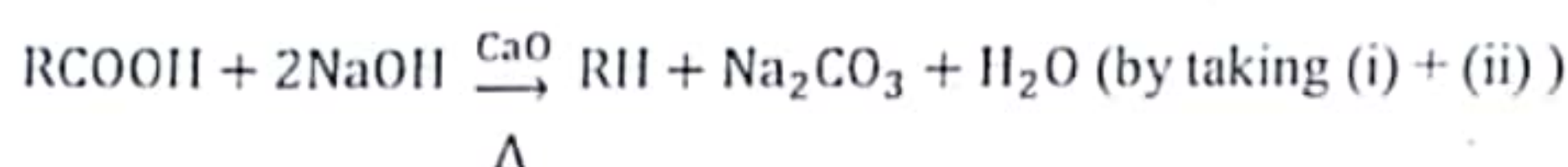
Sodium carboxylate is formed by mixing NaOH and carboxylic acid as per equation:



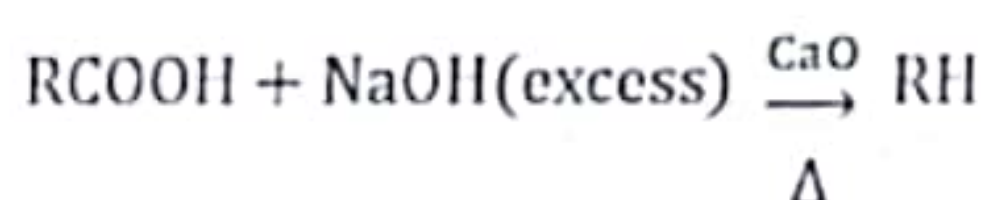
More addition of NaOH to the RCOONa in (i) above yields alkane (RH) as per equation:



Thus combining (i) and (ii), the equation for preparation of carboxylic acid from carboxylic salt is obtained.



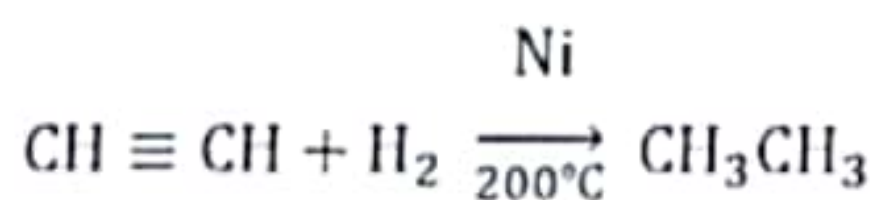
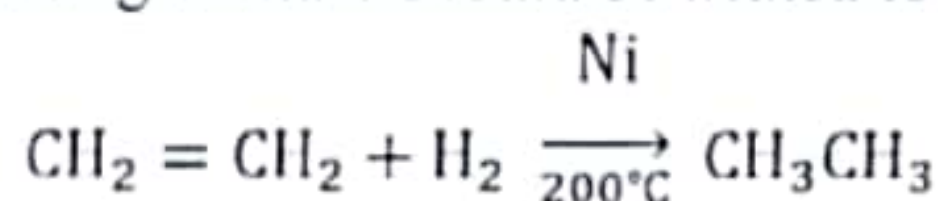
Or by considering organic product only, the equation may be re-written as:



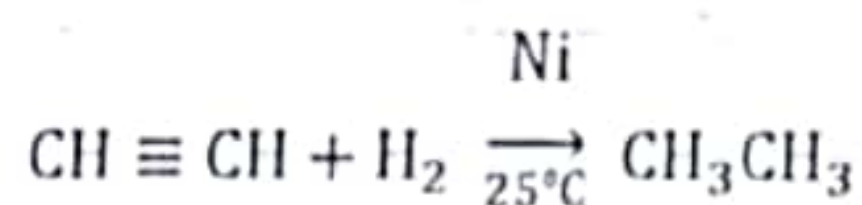
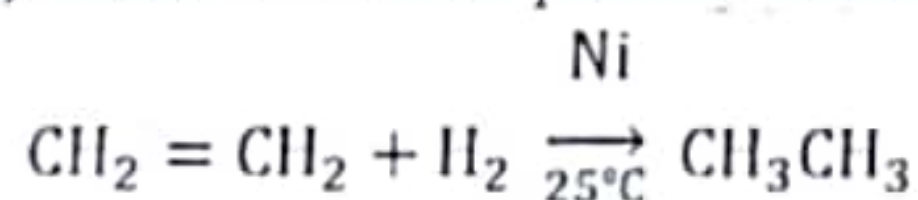
Hydrogenation of unsaturated hydrocarbons

Alkenes and alkynes undergo catalytic hydrogenation to give alkane. Nickel, platinum or palladium catalyst may be used.

- If nickel catalyst is used, the reacting mixture should be heated to temperature of about 200°C.

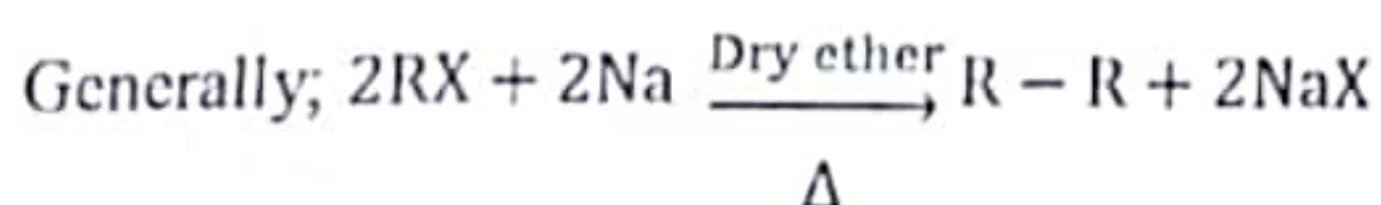


- If platinum or palladium is used, the reaction takes place at room temperature.

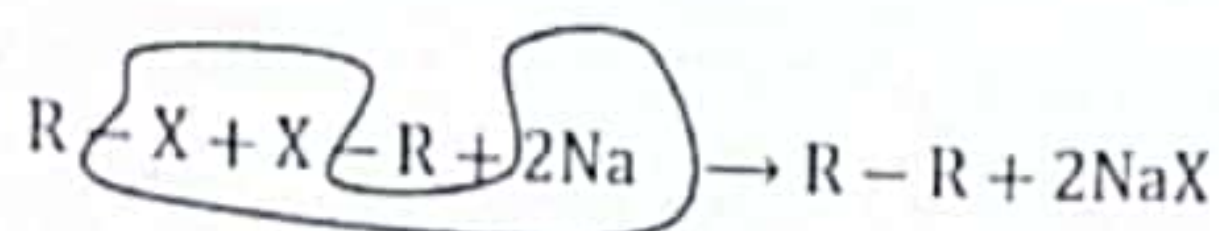


Wurtz reaction

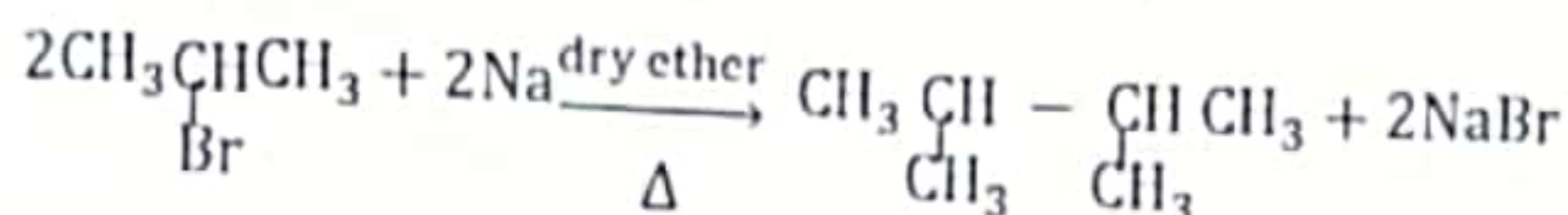
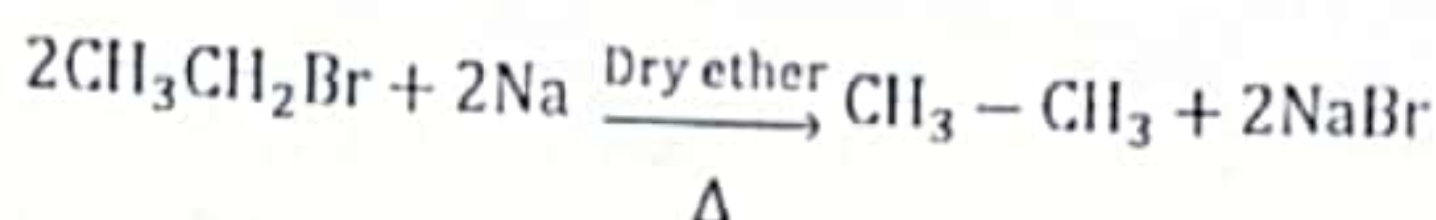
Wurtz reaction is the organic reaction between haloalkane and sodium under presence of dry ether to form alkane.



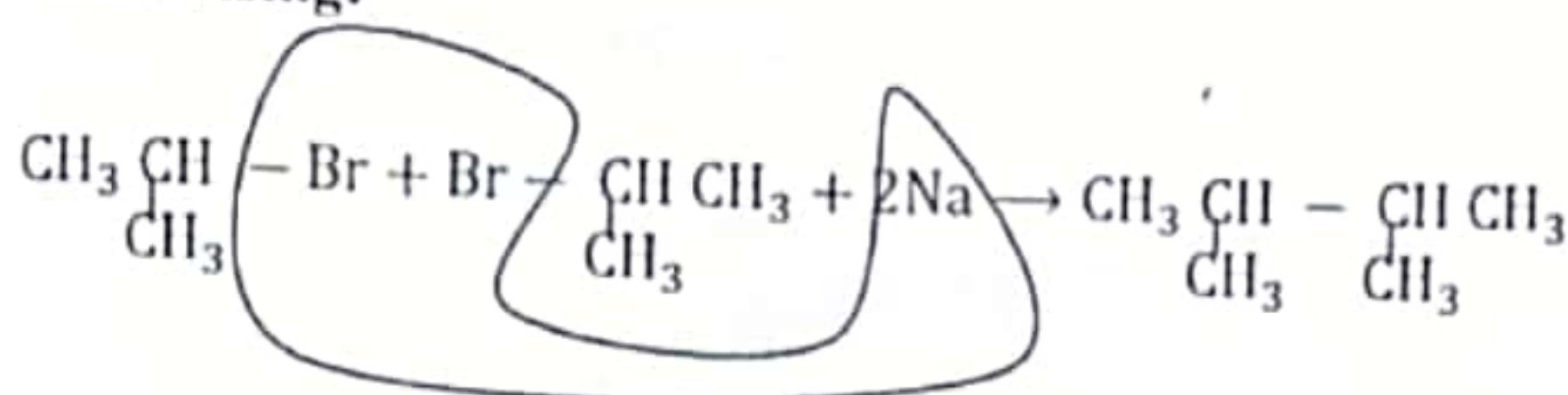
Memorising:



For example:



Memorising:



In the above reaction, ether must be dry because if it would be ether solution (moist ether), sodium would combine with water to form sodium hydroxide which in turn form alcohol (and alkene) with haloalkane and hence mixture of organic products occurs.

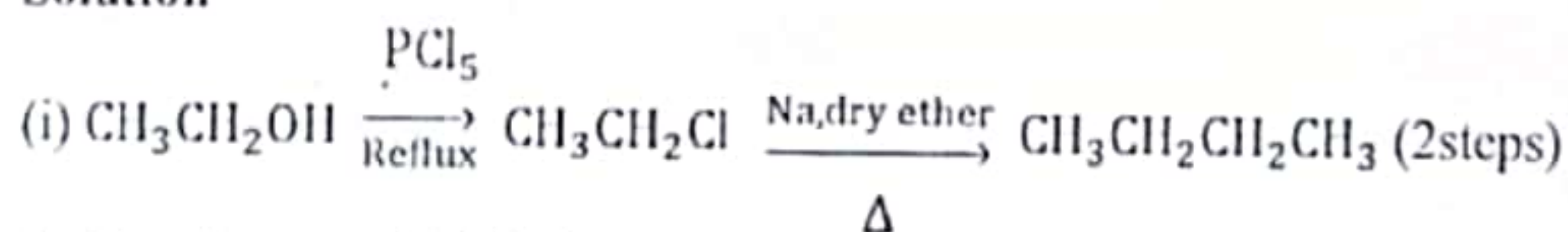
- Also in the above reaction it is clearly understood that number of carbon atoms is doubled in the reaction, so the reaction is very important in dealing with conversion problems which show that number of carbon atoms has doubled.

Example 4

Convert:

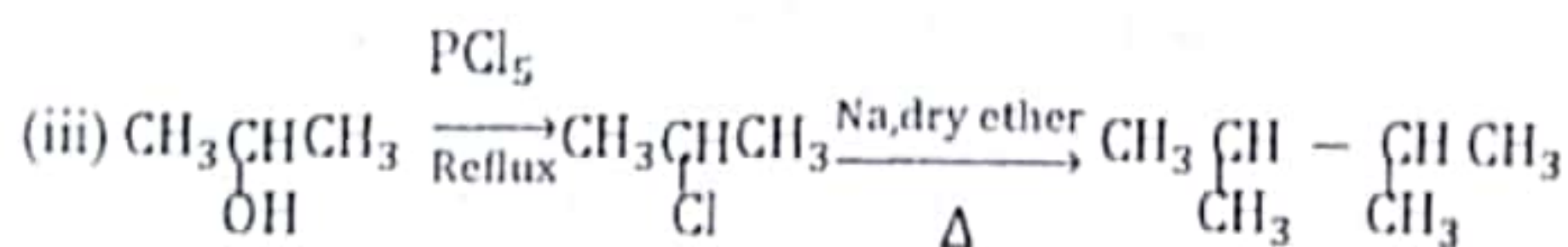
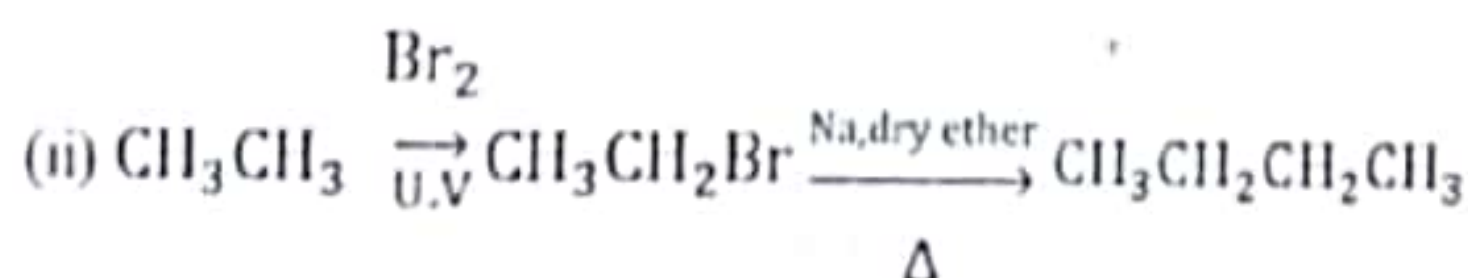
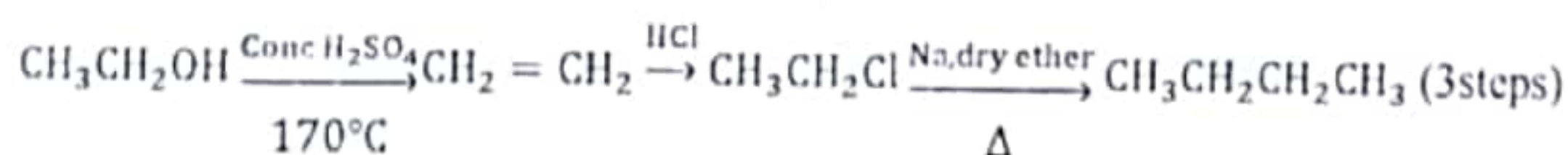
- CH_3CH_2OH into $CH_3CH_2CH_2CH_3$
- CH_3CH_3 into $CH_3CH_2CH_2CH_3$
- Propan-2-ol into 2,3-dimethylbutane

Solution



('Reflux' means distillation under condensation)

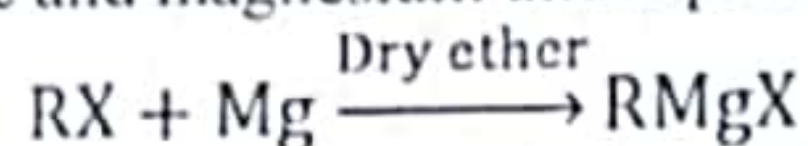
Alternatively:



Hydrolysis of Grignard reagent

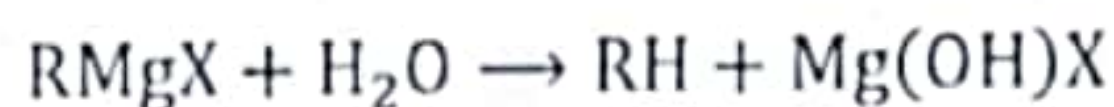
Grignard reagents are organic compounds with general formula of $RMgX$ (alkyl magnesium halide) where R represents any group of hydrocarbon and X is halogen.

- It is prepared by mixing haloalkane and magnesium under presence of dry ether.

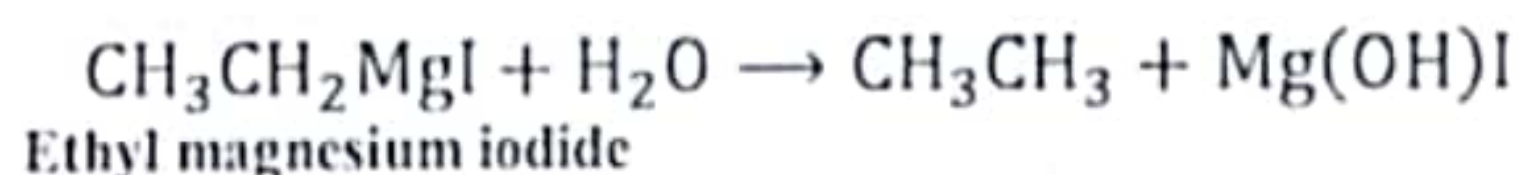


If X is iodine, the grignard reagent becomes most reactive and therefore alkyl or aryl magnesium iodide is the most preferred grignard reagent

Generally;



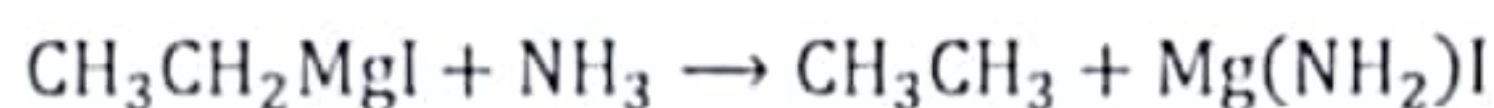
For example,



The reader should understand that:

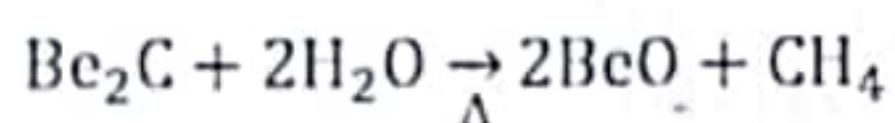
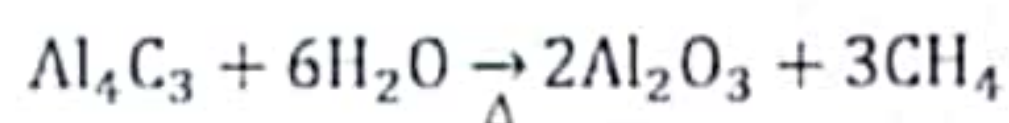
Grignard reagent always undergo double decomposition with water or with other compounds having active hydrogen (the hydrogen attached on O, N, F or triple bonded carbon atom are known as active hydrogen) to give alkane.

For example;

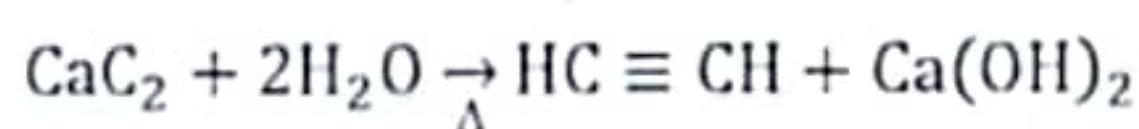


Hydrolysis of aluminium or beryllium carbides

Only methane, CH₄ can be obtained by the hydrolysis of Be or Al carbides

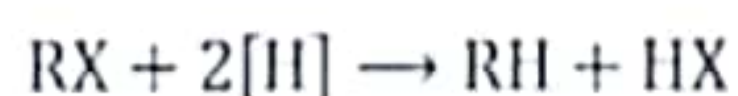


But hydrolysis of calcium carbide gives ethyne.



Reduction of haloalkane

Haloalkanes on reduction with nascent hydrogen to form alkanes.



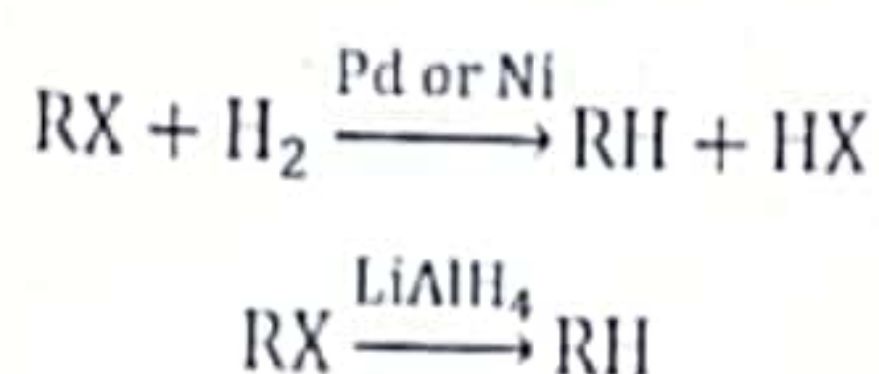
Where [H] represents nascent hydrogen.

- The nascent hydrogen may be obtained by any one of the following:
 - Zn + HCl
 - Zn + CH₃COOH
 - Zn-Cu couple in ethanol
 - Red P + HI
 - Al-Hg + ethanol (aluminium amalgam in ethanol)

For example;



Alkyl halides can also be reduced catalytically to alkane by H_2 | Pd or $LiAlH_4$ or by H_2 | Ni.

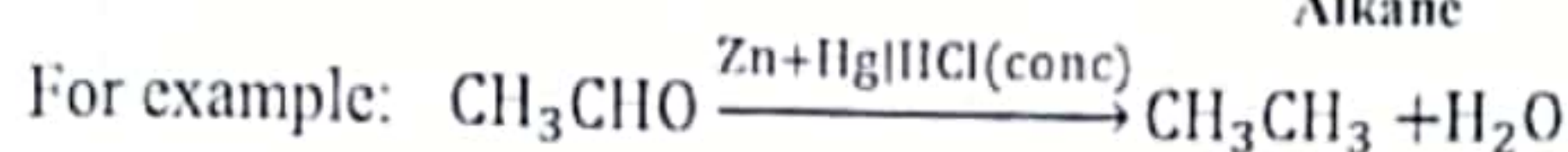
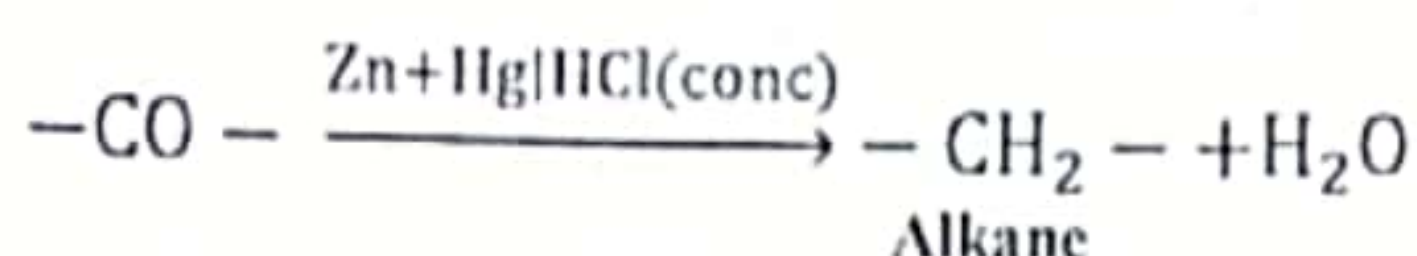


Reduction of carbonyl compounds

Both aldehydes and ketones can be reduced to alkane. The reduction can be done by one of the following three ways.

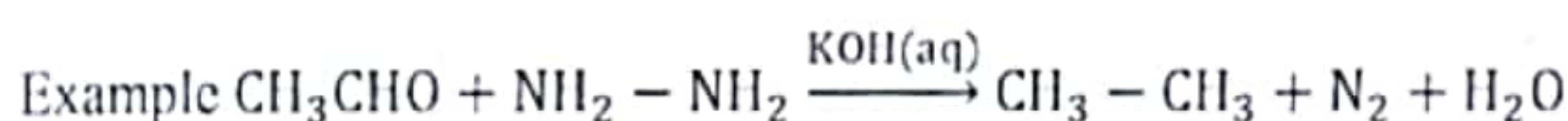
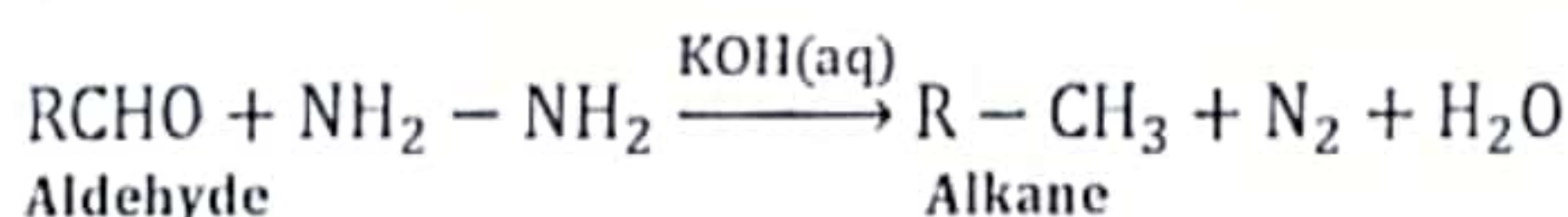
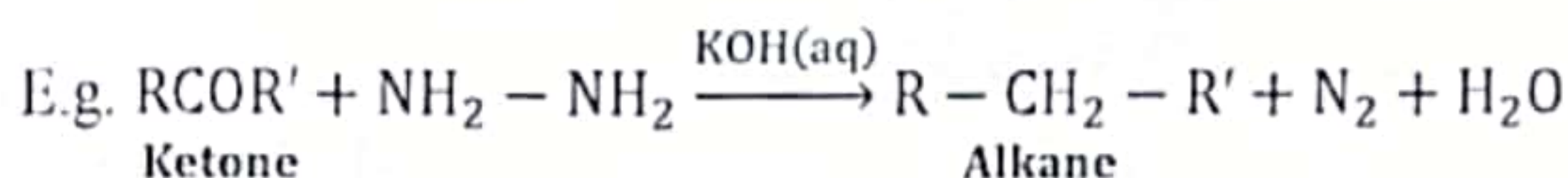
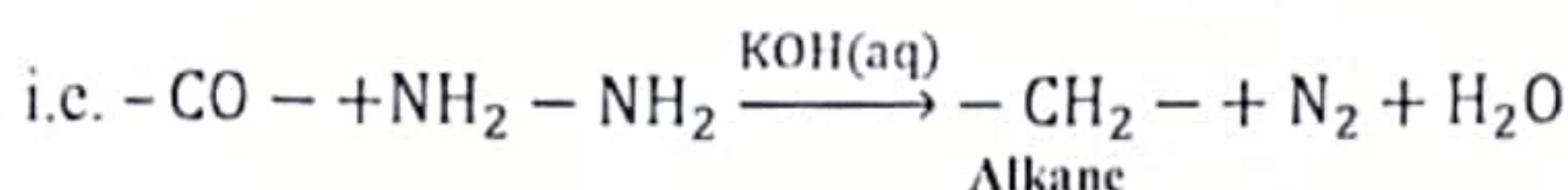
1. Clemmensen reduction

This is the reduction of carbonyl compounds by zinc amalgam and concentrated hydrochloric acid.

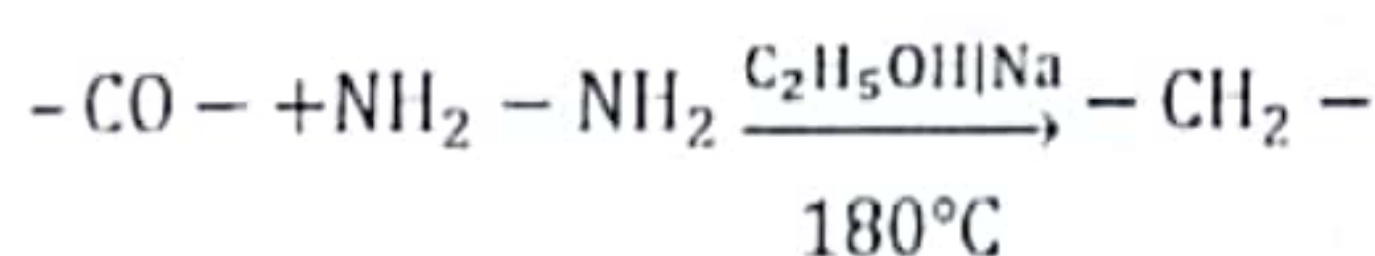


2. Wolf Kishner reaction

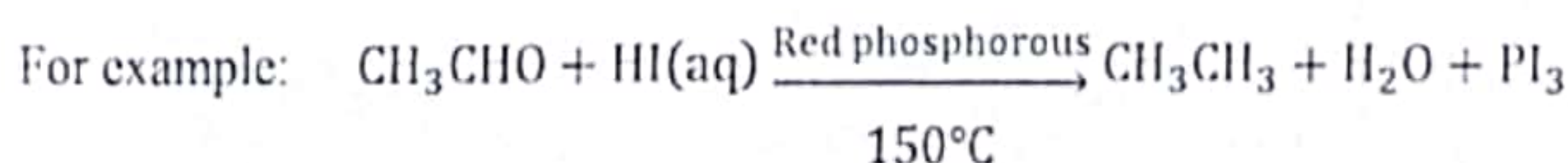
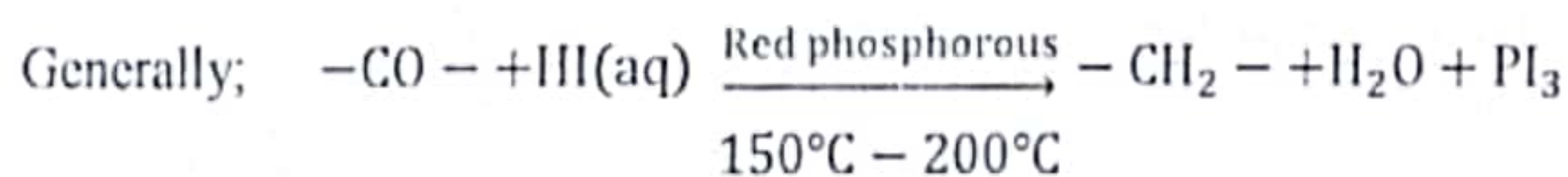
Under presence of strong alkaline solution like KOH, carbonyl compounds reacts with hydrazine ($NH_2 - NH_2$) to give corresponding alkane and the reaction is known as **Wolf Kishner reduction**.



Mixture of ethanol and sodium heated to $180^\circ C$ can be used instead of $KOH(aq)$

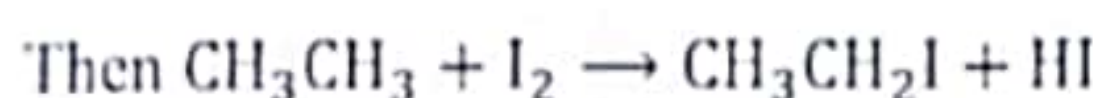
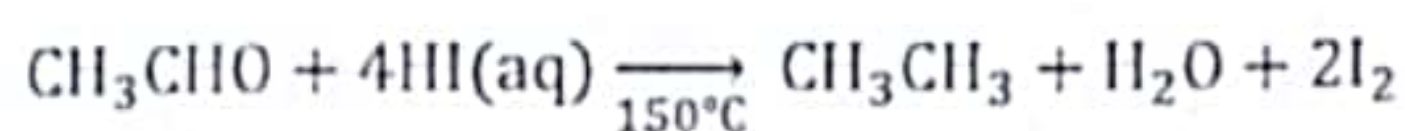


3. By using HI under presence of red phosphorous



What will happen if red phosphorous is absent?

If the phosphorous would be absent, the produced alkane would undergo further reaction with liberated iodine to form iodoalkane.



But in presence of the phosphorous, the liberated iodine reacts with it to give phosphorous triiodide hence preventing formation of iodoalkane. $2\text{P} + 3\text{I}_2 \rightarrow 2\text{PI}_3$

So the significance of the red phosphorous in the reaction is to prevent formation of iodoalkane.

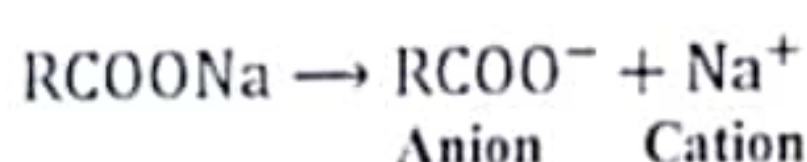
It should be noted that:

Alcohol, carboxylic acid and its derivation also react with hydroiodic acid under presence of red phosphorous to give alkane as carbonyl compounds do.

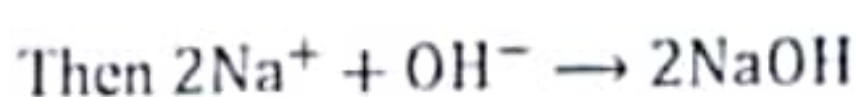
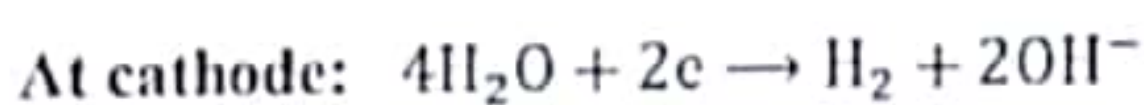
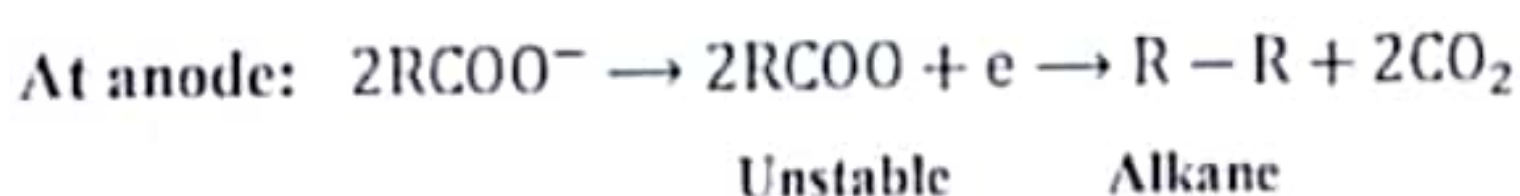
Kolbe electrolysis reaction

Alkanes are formed, on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated mono carboxylic acids, i.e. RCOONa or RCOOK .

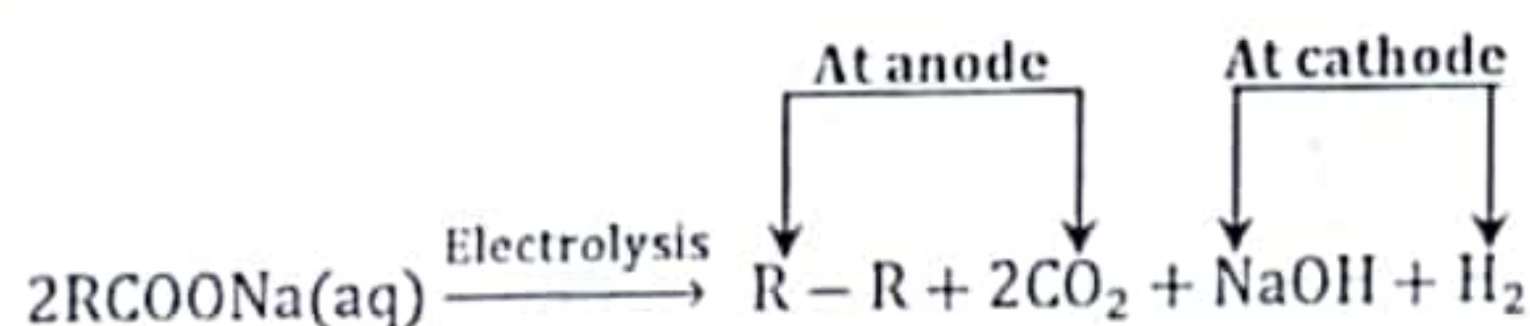
- Taking RCOONa as an example, its ionic composition is as follows:



During electrolysis, the following electrode reactions occur:



Hence the overall reaction equation becomes:



CHEMICAL REACTIONS OF ALKANES

Among hydrocarbons, alkanes are least reactive as result of their saturated nature.

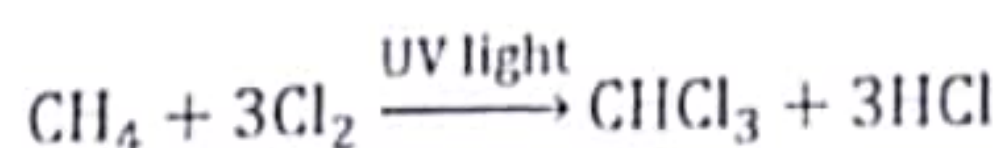
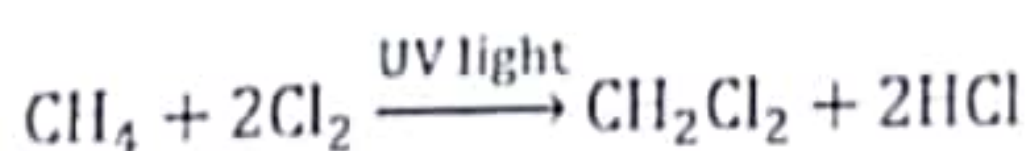
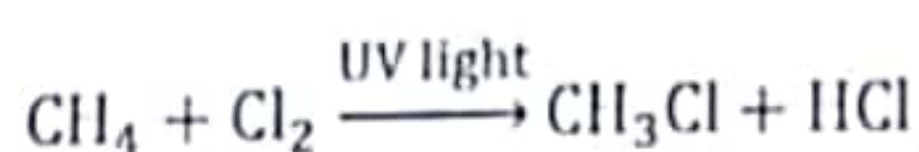
- However alkanes undergo the following organic reactions:

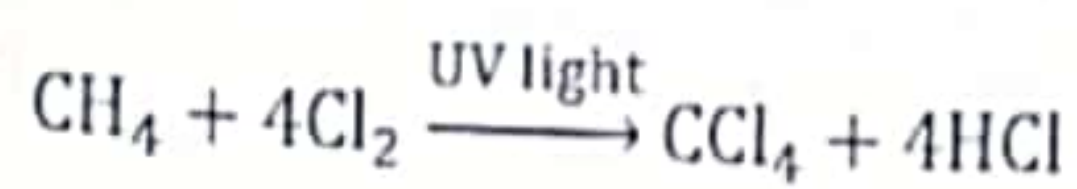
- Free radical substitution reactions
- Combustion
- Cracking
- elimination reaction
- Nitration

Free radical substitution reactions

Alkanes undergo free radical substitution reaction with halogens under presence of very high temperature or ultraviolet (UV) light

For example:



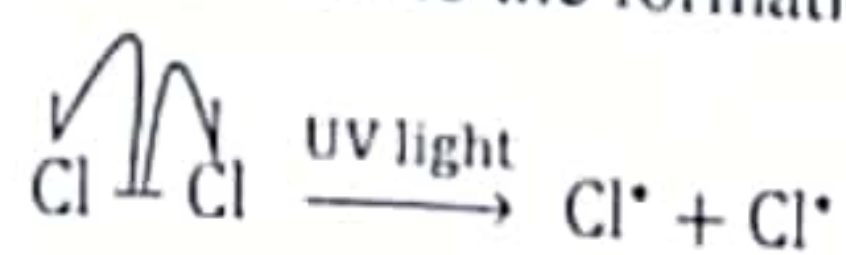


Mechanism of this reaction follows three steps, namely:

- i. Initiation step
- ii. Propagation step and
- iii. Termination step

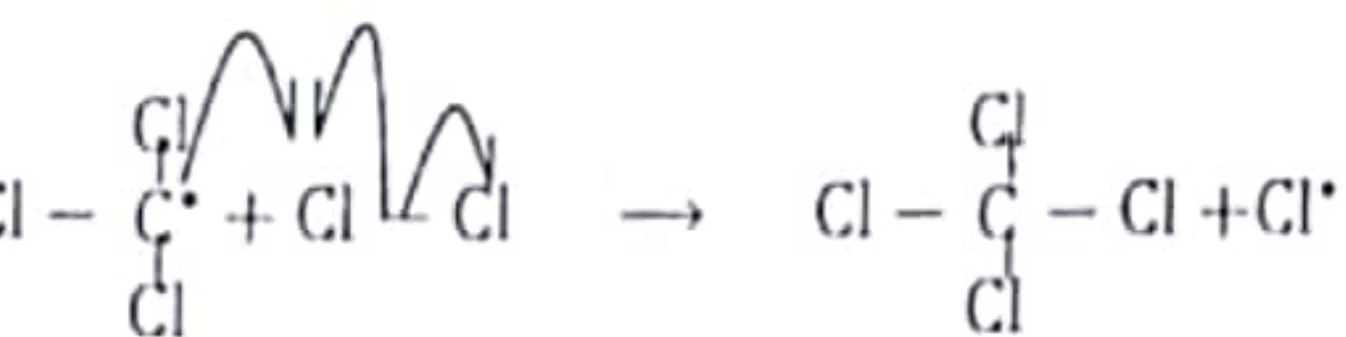
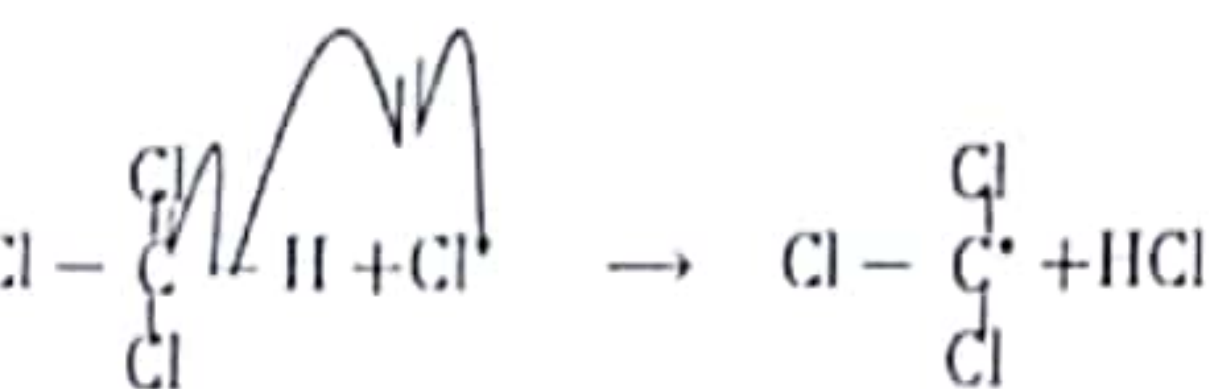
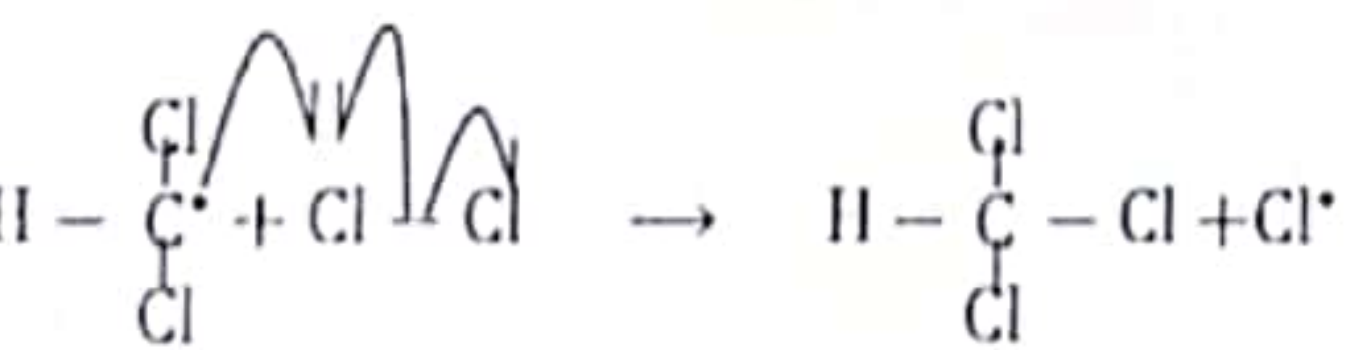
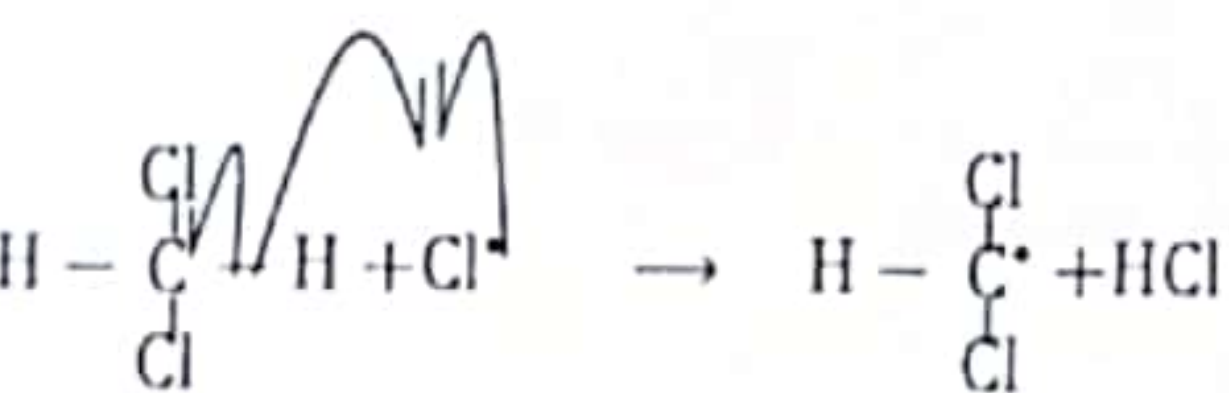
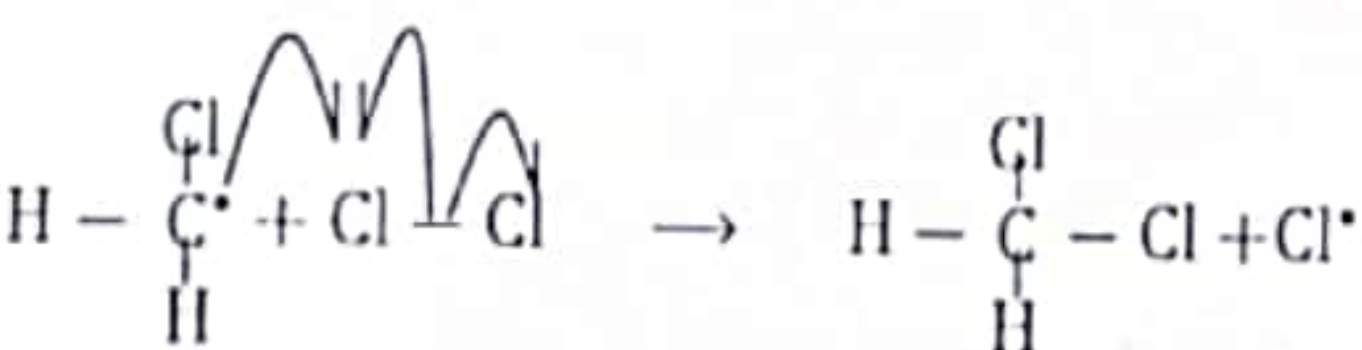
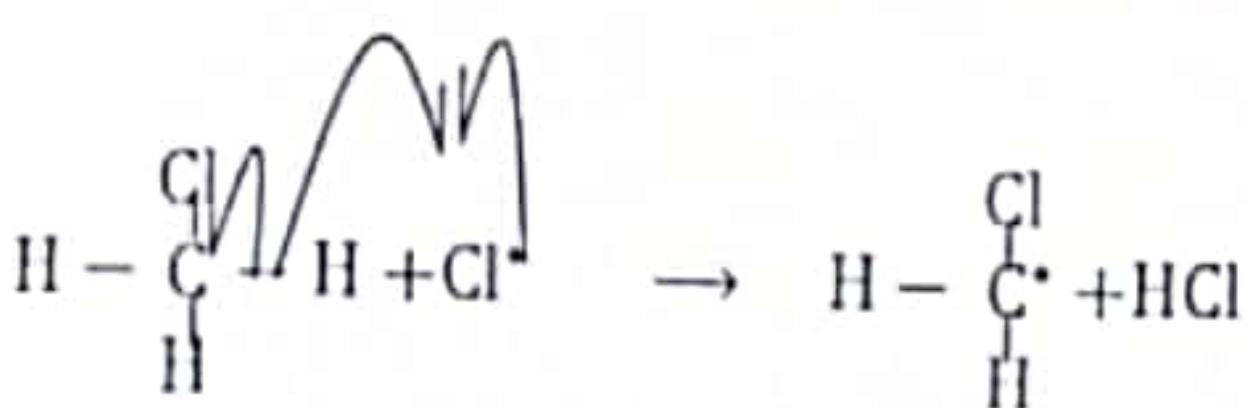
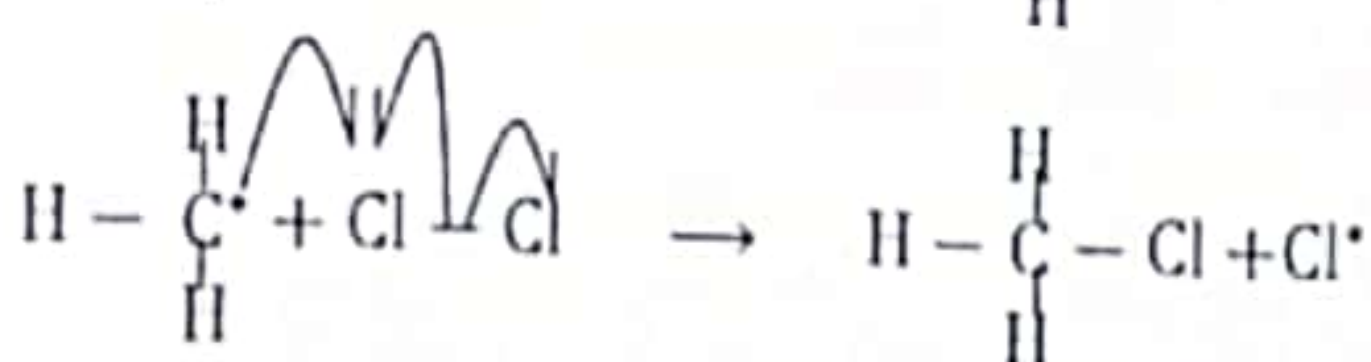
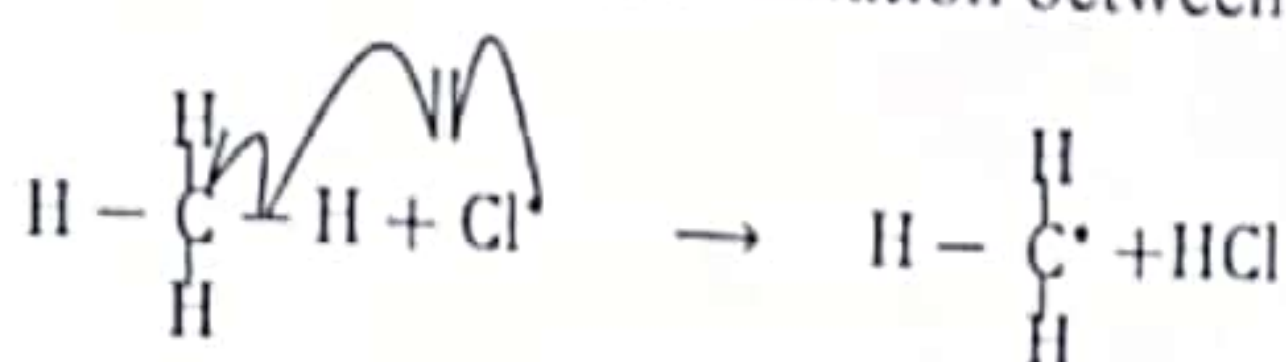
1. Initiation step

This involves the formation of free radicals.



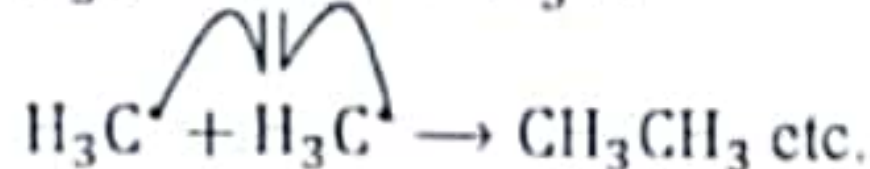
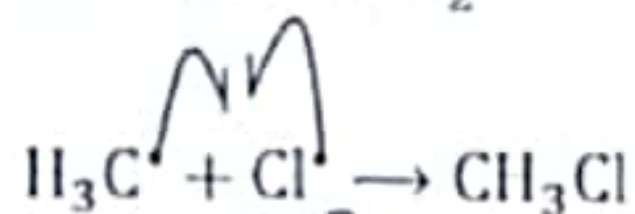
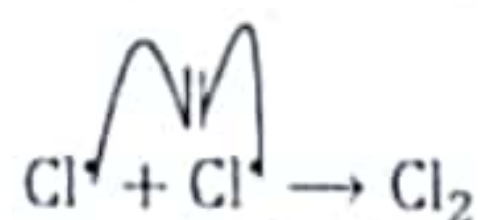
2. Propagation step

This involves the combination between free radicals and molecules.



Termination step

This involves the combination of free radicals to form molecules.



The overall reaction equation is obtained by adding all elementary reactions in the propagation step to get the following equation: $\text{CH}_4 + 4\text{Cl}_2 \xrightarrow{\text{UV light}} \text{CCl}_4 + 4\text{HCl}$

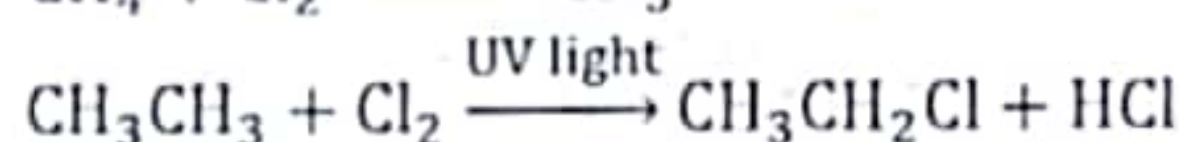
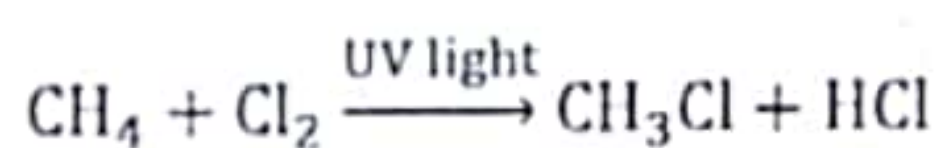
It should be noted that:

If CH_4 present in excess, the product becomes CH_3Cl and if Cl_2 present in excess, the product becomes CCl_4 .

Free radical substitution reaction in alkane with more than two carbons

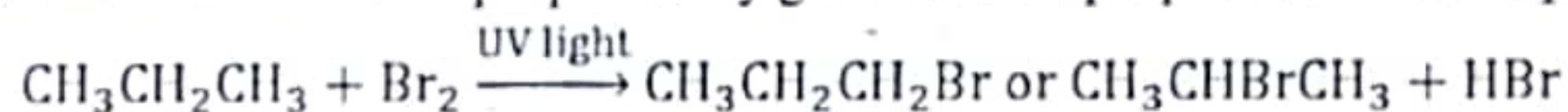
When methane and ethane is mono-halogenated only single product is formed.

- For example, monochlorination of methane gives chloromethane while that of ethane gives chloroethane.



But when alkane larger than ethane is halogenated, more than one product can be formed:

- For example mono-bromination of propane may give 1-bromopropane or 2-bromopropane.



Among the two products, one product has greater possibility of occurring and the product is known as a **major product** and another product with smaller possibility of occurring is known as **minor product**. Now the question is....., *what factors determine formation of the major product?*

The important factors to discuss here are:

- Stability of intermediate free radical
- Selectivity of halogens

Stability of intermediate free radical

Consider the example of mono-bromination of propane.

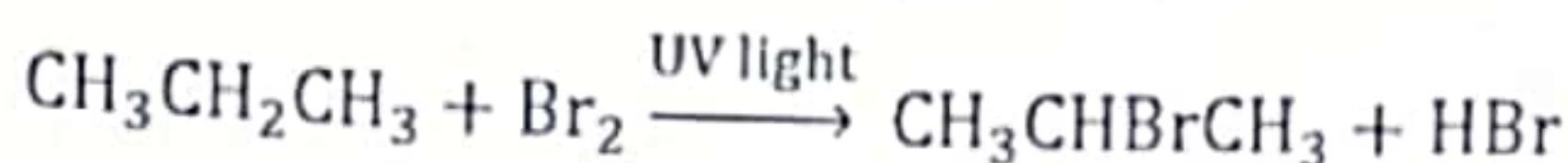
- In the propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, there are 6 primary hydrogens and 2 secondary hydrogens out of total of 8 replaceable hydrogens.
- So one may predict the percentage of 1-bromopropane which is formed after substituting primary hydrogen to be 75% $\left(\frac{6}{8} \times 100 = 75\%\right)$ and that of 2-bromopropane which is formed after substituting secondary hydrogen to be 25%.
- However practically, it has been found that the percentage of 2-bromopropane is 98% (not 25%!) while that of 1-bromopropane is only 2%! Very interesting.....! What is the reason behind this practical fact?

Practically the product with more stable intermediate free radical has greater possibility of existing and become the major product.

- If $\text{Br}^\bullet$ substitutes to the primary hydrogen the intermediate free radical becomes $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}$ which is primary free radical.
- If $\text{Br}^\bullet$ substitutes to the secondary hydrogen the intermediate free radical becomes $\text{CH}_3\dot{\text{C}}\text{HCH}_3$ which is secondary free radical.

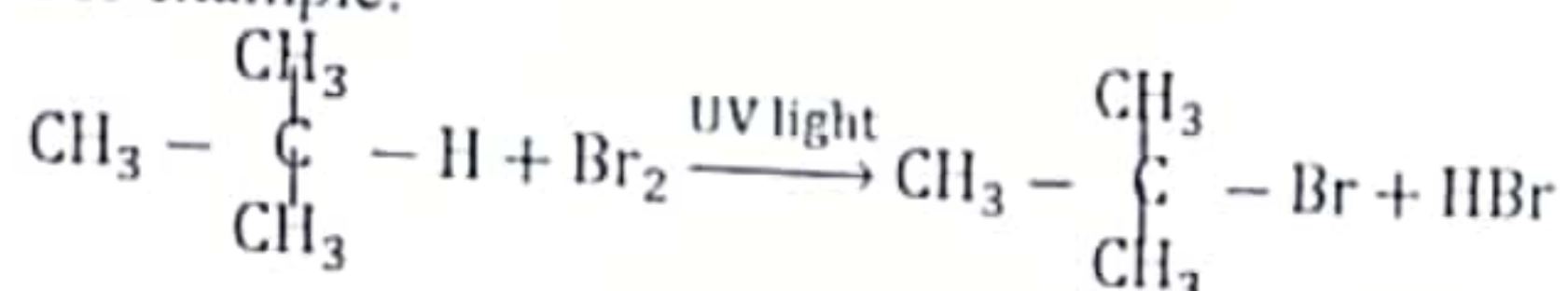
Since secondary free radical is more stable than primary free radical, the secondary hydrogen becomes more reactive favouring substitution in it and hence 2-bromopropane becomes the major product.

- Therefore by writing the major product only, the reaction equation for mono-bromination of propane is;



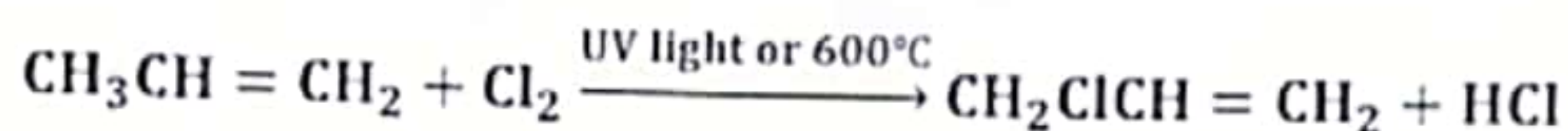
For similar reasoning, tertiary hydrogen is more reactive than both secondary and primary hydrogen (as tertiary free radical is more stable than secondary free radical).

- For example:



It should be noted that:

- Stability of intermediate free radical also explains why propene reacts with chlorine gas at very high temperature or UV light to give 3-chloropropene.

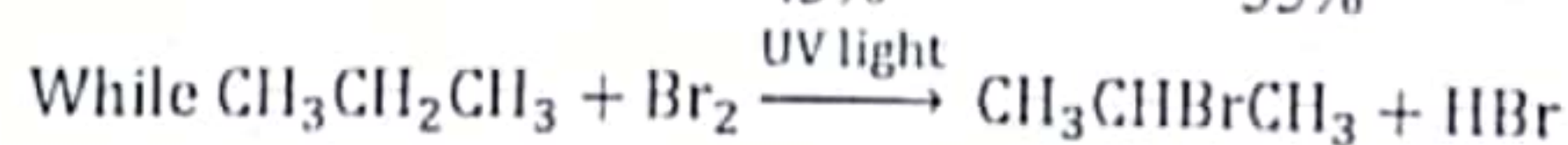
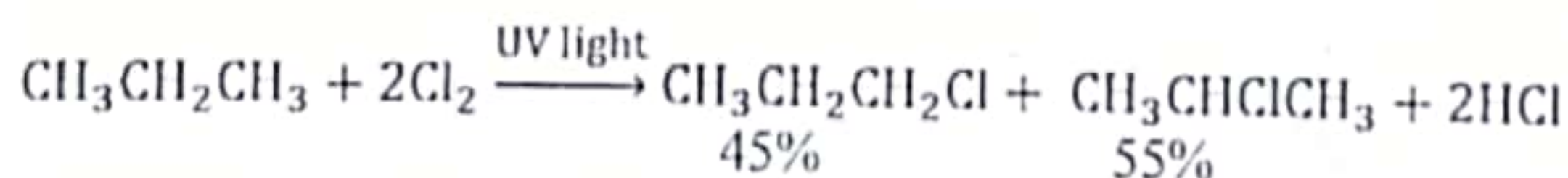


Selectivity of halogens

When halogen is very reactive, it can substitute even to less reactive hydrogen. In other words, **reactive halogen is said to be less selective to hydrogen** it substitute (It is like when you are hungry, i.e. more reactive to food, you become less selective to kind of food to eat!)

- The reactivity of the halogens decreases in the following order:
 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Important halogens to discuss here are chlorine and bromine, since fluorine is so explosively reactive that it is difficult to control, and iodine is generally unreactive.

Chlorine being more reactive than bromine has lower selectivity and this explains why mono-chlorination of propane gives both primary and secondary product unlike mono-bromination of the same compound which gives almost secondary product only

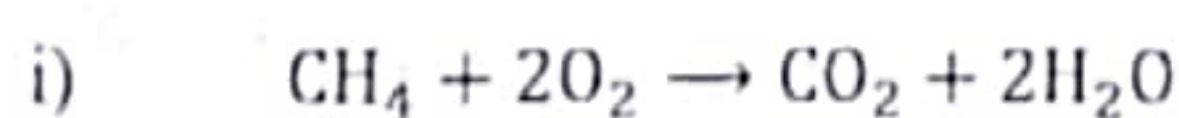


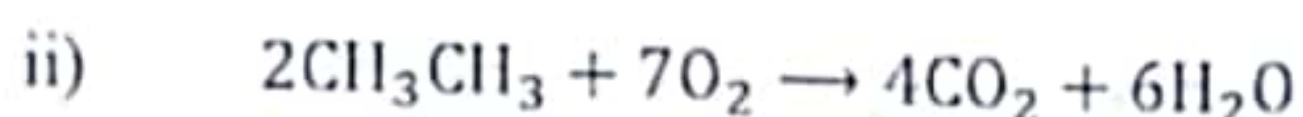
Thus as the selectivity decreases, the percentage of primary product starts to rise up towards the hypothetical percentage of 75% of the primary product.

Combustion

Alkanes burn in oxygen to give carbondioxide and water.

For example:





Combustion reaction is highly exothermic.

- The heat energy released in the combustion may be used for direct heating e.g. candles. It can also be converted into mechanical energy (e.g. cars, lorries, ships), or even electrical energy (e.g. power stations) and hence alkanes are commonly used as **fuels**. A **Fuel** is a something that can be changed in a reacting vessel to produce useful energy.

Complete and incomplete combustion

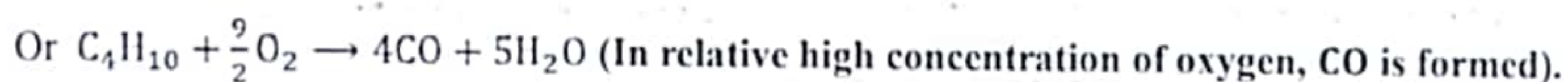
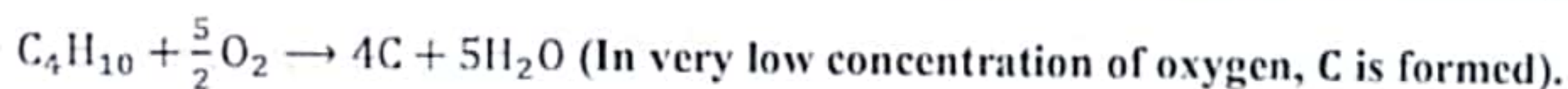
Complete (or efficient) combustion of alkane (or any hydrocarbon) produces CO_2 and H_2O while **incomplete** (inefficient) combustion produces CO , C and H_2O . *What factors determine the efficiency of combustion?*

Along with other factors, the following factors are useful in determining whether the combustion will be complete or incomplete.

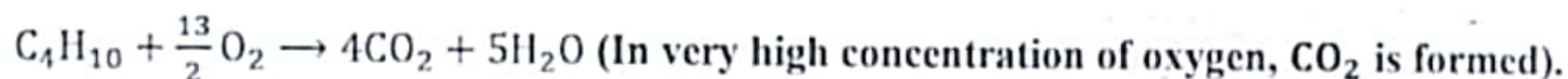
- Concentration of oxygen (air)
- Hydrogen to carbon ratio
- Number of branches in the combustible compound

Concentration of oxygen

- Incomplete combustion occurs when there is a little supply of oxygen (air). For example;



- Presence of excess oxygen ensures complete combustion.

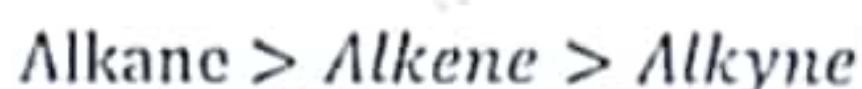


Hydrogen to carbon ratio

Since hydrogen, H , is more combustible than carbon, C , alkane with large $\text{H}:\text{C}$ ratio is more combustible. For example, with $\text{H}:\text{C}$ ratio of 6:2 or 3:1, C_2H_6 is more combustible than C_2H_4 which has $\text{H}:\text{C}$ ratio of 4:2 or 2:1.

- Hydrocarbons with large $\text{H}:\text{C}$ ratios are more likely to undergo complete combustion to give a blue flame.
- On another hand, hydrocarbons with small $\text{H}:\text{C}$ ratios are more likely to undergo incomplete combustion to give a yellow smoky flame.

Among three classes of aliphatic hydrocarbons, alkanes having greatest $\text{H}:\text{C}$ ratio have greatest ability of undergoing complete combustion followed alkene and the last is alkyne which is most likely to undergo incomplete combustion.



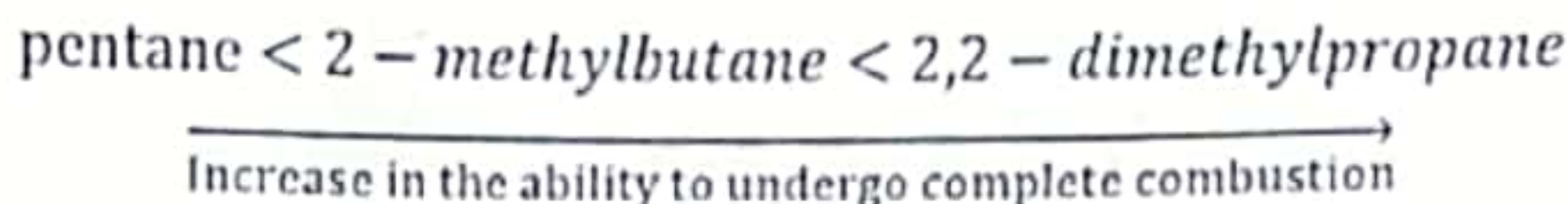
↓
Decrease in the ability to undergo complete combustion

Number of branches in the combustible compound

For two isomeric alkanes, the more branched alkane has more efficient combustion than the less branched one.

- This is simply because the more branched hydrocarbon has smaller surface area and hence weaker Van-der-waals force of attraction.

As an example efficiency of combustion of some isomers of pentane is accordance to the following order:



What are problems of incomplete combustion of the alkane as fuel?

The less oxygen that is available and the less branched alkane is, the more likely it is that incomplete combustion will occur. This is a particular problem in internal combustion engines where the air supply is limited.

- Incomplete combustion is a problem for three reasons:
 - Less energy is released by incomplete combustion than by complete combustion.
 - Carbon monoxide is a pollutant – it is absorbed by the blood in place of oxygen, and hence reduces the ability of the blood to carry oxygen causing suffocation and eventually death.
 - Carbon particles as soot can cause breathing difficulties and cancer.

It is therefore desirable to ensure that the **air supply is as good as possible** and the **straight alkane should be converted to the branched one** when burning alkane fuels.

Cracking

Cracking is a chemical process in which larger hydrocarbon molecules are broken down at high temperatures, with or without catalysts, to produce smaller hydrocarbon molecules.

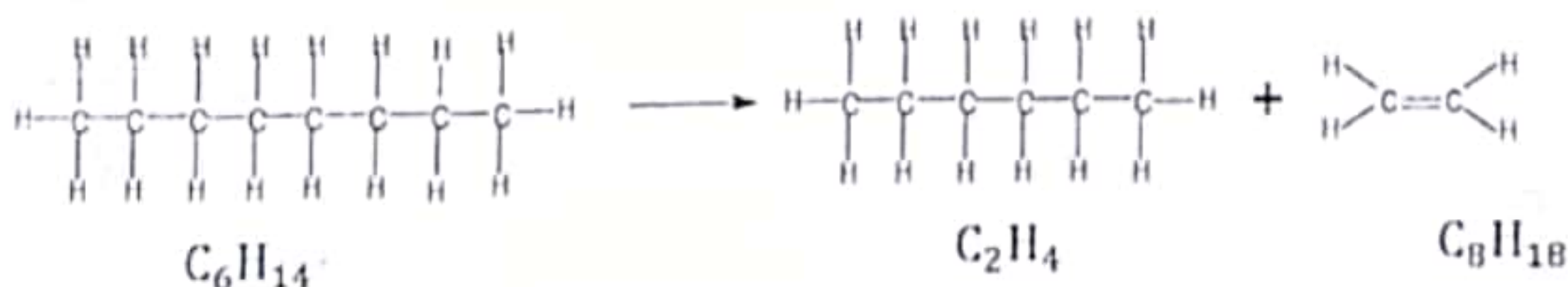
- Cracking can be grouped into three types, namely:
 - Thermal cracking
 - Catalytic cracking
 - Hydrocracking

Thermal cracking

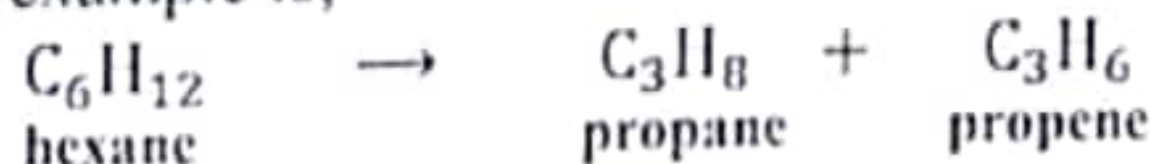
In thermal cracking, the bonds are broken using a **high temperature** (400°C – 900°C) and a **high pressure** (70 atmospheres).

- When higher member of alkanes are allowed to undergo thermal cracking lower members of alkanes and smallalkenes are formed.

In most cases, thermal cracking makes molecule to break near the end of the chain, giving a **high percentage of small alkenes** such as ethene. For example:



Another example is;



Since thermal cracking **decomposes** hydrocarbon by application of heat, it is also known as **pyrolysis**. *Pyrolysis is the decomposition of a compound on heating in absence of air.*

It should be noted that:

There is not any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds.

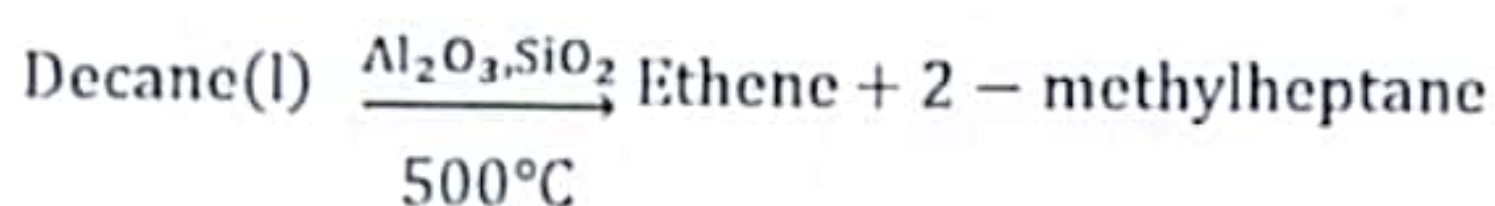
Catalytic cracking

In catalytic cracking, the bonds are broken using a **high temperature** (450°C, which is generally lower than in thermal cracking), a **slight pressure** (slightly greater than 1 atmosphere), and a **zeolite catalyst** (A type of clay containing Al_2O_3 and SiO_2).

- So catalytic cracking is cheaper and more efficient than thermal cracking as it uses a lower temperature and pressure.

The zeolite catalyst favours the formation of branched alkanes and cycloalkanes, which are widely used in **motor fuels**.

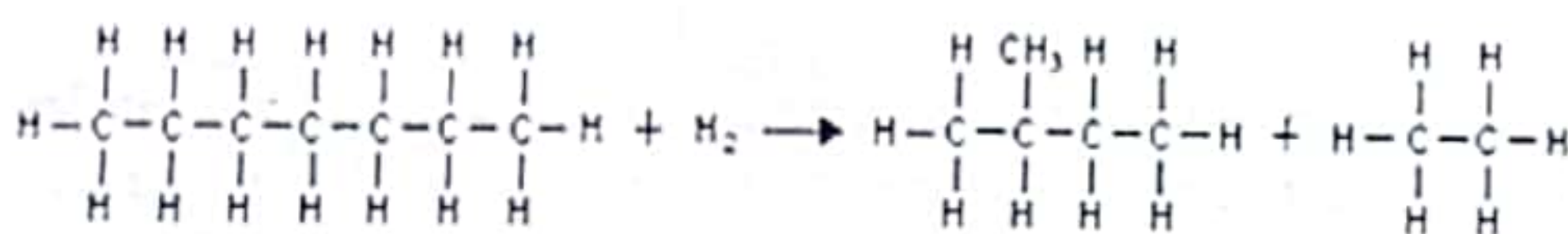
- The most important product of catalytic cracking is 2-methylheptane, which is the major component of petrol.



Hydrocracking

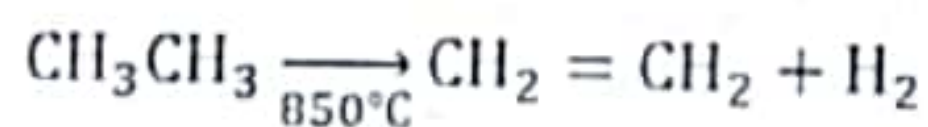
Hydrocracking is a process by which the hydrocarbon molecules are broken into simpler molecules by the addition of hydrogen under high pressure and in the presence of a catalyst.

- It is the combination of catalytic cracking and hydrogenation. For example;



Elimination reaction (dehydrogenation)

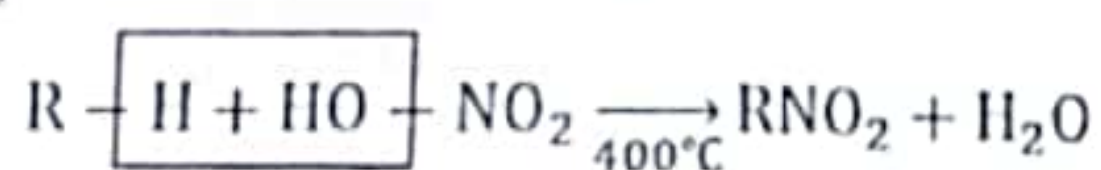
When ethane is heated to temperature of about 850°C, ethene is formed.



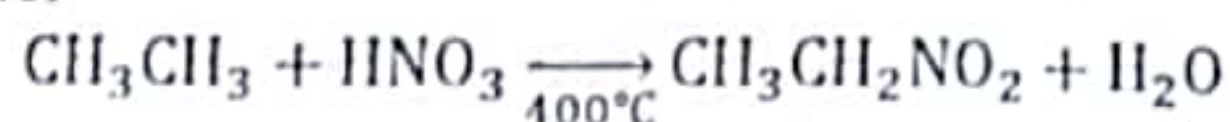
Nitration

Alkanes react with nitric acid to give nitroalkanes.

Generally;



Example:



MANUFACTURE OF ALKANE

Extracted hydrocarbons in a liquid form are referred to as **crude oil**, **mineral oil** or **petroleum** (literally "**rock oil**" from Latin words 'petra' which means 'rock' and 'oleum' which means 'oil') whereas hydrocarbons in a gaseous form are referred to as **natural gas**.

- Natural gas and crude oil are main sources of alkane. They were formed when dead marine animals and plants died and sank to the bottom of ancient seas and were covered with sediments in an anoxic environment (an environment without oxygen) and converted over many millions of years at high temperatures and high pressure to their current form.

Production of alkane from natural gas

In large proportion, natural gas contains **methane** (has greatest proportion) and **ethane**, with some **propane** and **butane**.

- Raw natural gas often contains impurities that make it '**sour**' as it contains the very toxic gas hydrogen sulphide, which forms acidic solutions when mixed with water. *The natural gas with significant amount of hydrogen sulphide gas is known as **sour natural gas**.*
- The hydrogen sulphide gas (also called rotten-egg gas) is poisonous. Exposure to only a small quantity of this gas is deadly.

Mining the natural gas

Natural gas is removed from underground by drilling a deep hole into the ground where geologists have predicted that natural gas is to be found.

Refining of natural gas

(i) Removing liquids

At the plant, water and liquid hydrocarbons are removed by physical means from the gas before it is chemically refined in an absorber tower.

(ii) Removing hydrogen sulphide and carbondioxide gas

During this process, the sour natural gas which contains acidic gases, hydrogen sulphide and carbondioxide gas reacts with an amine which is basic under relatively high pressure and low temperature in acid-base reaction.

- The amine "sweetens" the gas by removing any hydrogen sulphide (H_2S) and carbon dioxide gases, which are then released from the amine in a regenerator tower for further processing. *The natural gas which contains no hydrogen sulphide is known as **sweet natural gas**.*

(iii) Separation of components of natural gas

In most cases, the sweet natural gas is further refined into separate components. *How this is done?*

- At the refining plant, the sweet natural gas is cooled under high pressure (temperature of -100°C and pressure of 15atm to 50atm) to condense all the components except the methane gas.
- The condensed (liquid) portion is then slowly distilled to separate out the ethane, propane and butane fractions.

So finally only methane remains as the only gas component of the natural gas.

Production of alkane from crude oil

Crude oil is an important source of hydrocarbons whereby alkanes are predominant. It is a complex mixture with chain lengths of the hydrocarbons present varying from one to nearly one hundred carbon atoms.

- The actual components and their proportions vary from one field to another.

The refining of crude oil can be divided into two main types of processes:

- Physical processes and
- Chemical processes, such as cracking.

Physical processes

This can further be divided into:

1. Fractional distillation and
2. Solvent extraction

1. Fractional distillation

Fractional distillation is done in an apparatus called **fractionating column**.

- It is a tall tower (hence the name fractional distillation tower) which is hotter at the bottom of the tower and becomes cooler as you ascend towards the top of the tower. It contains trays positioned at various levels.

What happens when a crude oil is introduced into the fractionating column?

Different compounds in the crude oil have different boiling point due to difference in length of their carbon chain whereby the boiling point increases as number of carbons increases in the chain (recall melting and boiling point of hydrocarbon in the **chapter 9**).

- When crude oil is heated to 500°C in the absence of air, most of its constituent compounds vapourise. The compounds with boiling points higher than 500°C remain as mixtures called **asphalts and tars**.

The vapourised components of the crude oil rise and gradually cool in a metal tower. Due to difference in their boiling points, the compounds in the crude oil condense in different trays and this provides the basis of separating components of crude oil by fractional distillation.

- When the temperature of the liquids in the trays in the higher parts of the tower is below the boiling points of the vapourised compounds, the substances in the vapour begin to condense. Those substances with high boiling points condense in the lower, hotter trays of the tower, whereas those with lower boiling points condense in the cooler trays near the top of the tower. Side streams are withdrawn from various locations along the column. These various streams are called **fractions**. *Fractions are mixtures of hydrocarbons with similar boiling points.*

The fractions with the lowest boiling points generally contain the smallest molecules with few carbon atoms (short carbon chain).

- Below is the diagram of a typical fractionating column and a table showing the most important fractions and their main uses.

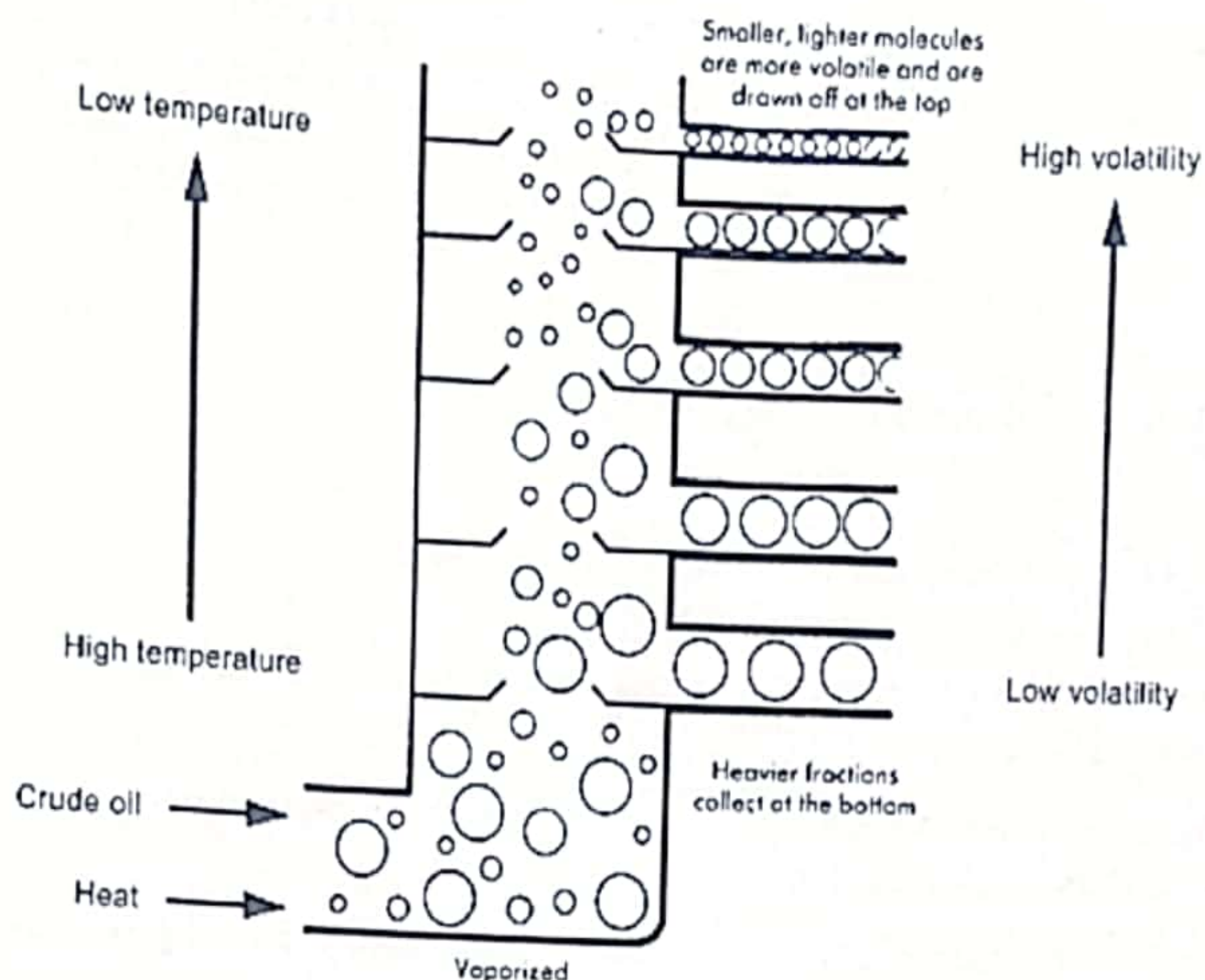


Figure: Fractionating column

FRACTION	USES	NUMBER OF CARBON ATOMS PER MOLECULE	BOILING POINT °C
Refinery gases: These are like natural gas in composition.	Stoves gas, Liquefied petroleum gas, LPG, (propane and butane)	1 to 4	Below 25
Petrol (gasoline)	Cars	4 to 12	20 to 200
Kerosine (paraffin)	Jet planes	9 to 16	175 to 275
Diesel oil	Trains	15 to 25	200 to 400
Lubricating oil	Lubrication	20 to 70	350
Fuel oil	Ships	30 to 40	350
Bitumen	Road surfaces	More than 50	Above 500

2. Solvent extraction

Fractions obtained from the fractional distillation tower are always contaminated with some impurities. Solvent extraction is always employed to remove these impurities.

- In the solvent extraction, a solvent is added to selectively dissolve and remove an impurity or sometime to separate some useful products from a mixture.

Chemical processes

Although all of the fractions produced from crude oil have their uses, the fractional distillation of crude oil does not produce enough of the light (small sized) hydrocarbons that are in demand (particularly the gasoline fraction) and produces too much of the heavier fractions which are less demanded.

- Chemical treatment of products obtained from fractional distillation is commonly applied to solve the problem. It involves the following processes:
 - Cracking
 - Catalytic reforming and alkylation

Cracking

Cracking reactions are like decomposition reactions because the main objective is to break larger molecules into smaller ones.

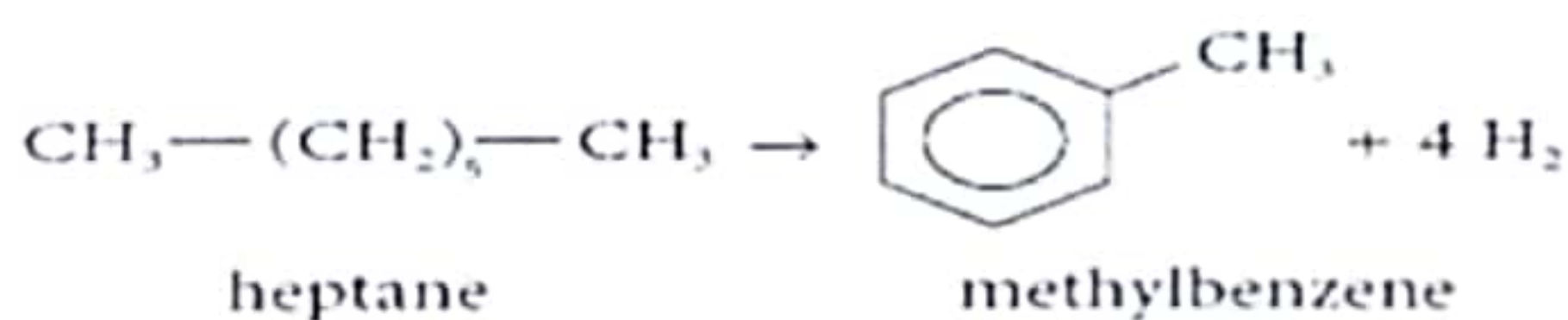
- So the reaction is very useful in converting heavier hydrocarbons into lighter ones. It may be thermal, catalytic cracking or hydrocracking.

Catalytic cracking has added advantage over thermal cracking because it can produce branched hydrocarbons which combust more efficient than unbranched ones thus making them better fuel. Furthermore catalytic cracking is more economical because it employ low pressure unlike thermal cracking which employ very high pressure (70atm) and it is very cost to build the apparatus for providing such large pressure.

Catalytic reforming and alkylation

Catalytic reforming is the chemical process involved in converting molecules in a naphtha (gasoline) fraction into aromatic gasoline molecules.

- These aromatic hydrocarbons have better burning properties than the original aliphatic (non-aromatic) molecules. A catalyst based on platinum and/or rhenium metal is used for this purpose.

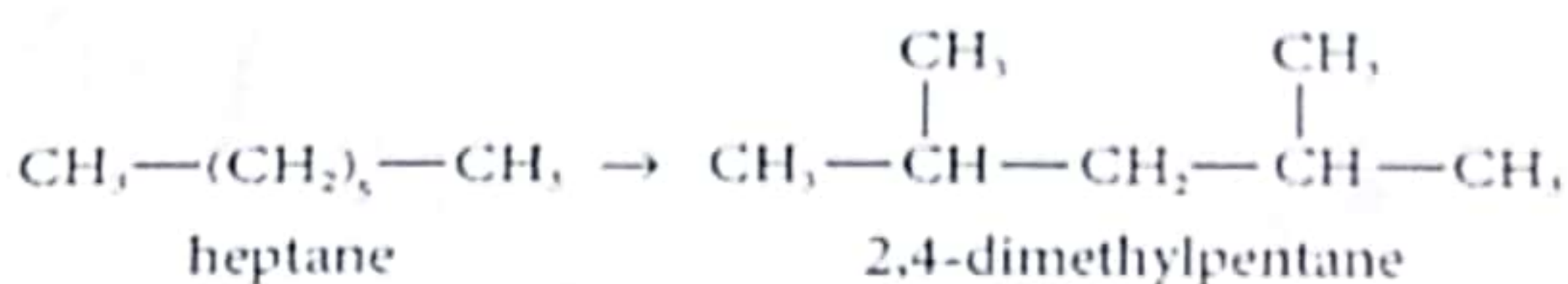


Alkylation

Another way of improving the quality of gasoline is to increase the branching of the molecules in a process called **alkylation**.

- This process is also called **isomerisation** because it converts a molecule with unbrached carbon chain into a branched isomer. Anhydrous aluminium chloride catalyst can be employed for this purpose.

For example, heptane can be converted into 2,4-dimethylpentane, a molecule that burns better (it has greater ability to undergo complete combustion) in an internal combustion motor.



To conclude, chemical process in refining of crude oil has the following practical advantages:

- It converts low-demand heavier fractions into higher demand fractions (through cracking).
- It makes useful hydrocarbons not naturally found in crude oil (through catalytic reforming and alkylation).

The reader should understand that:

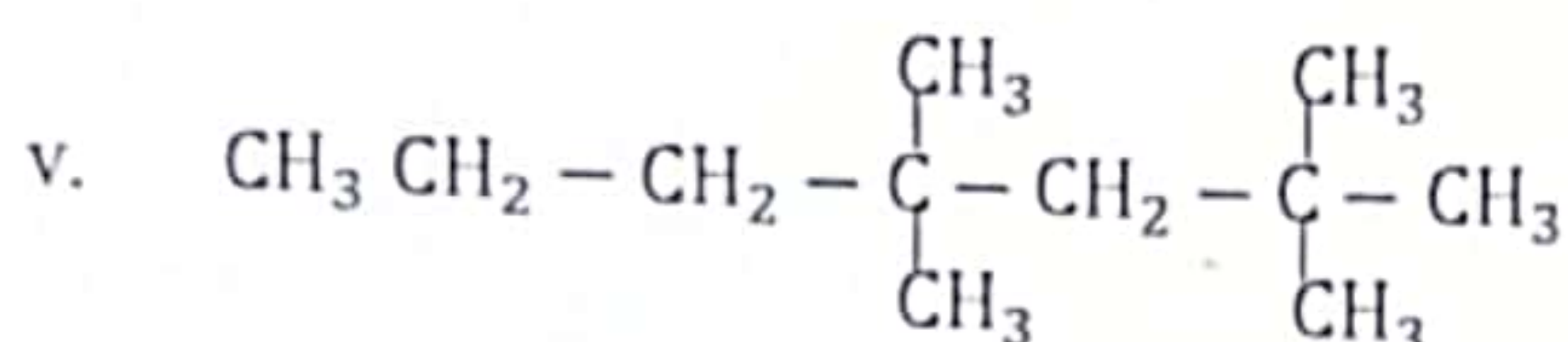
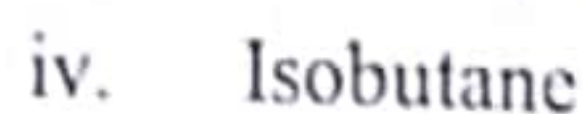
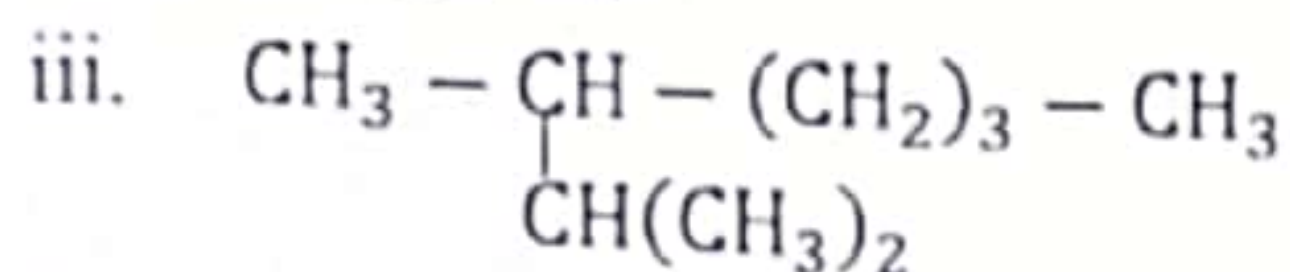
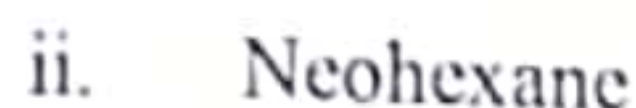
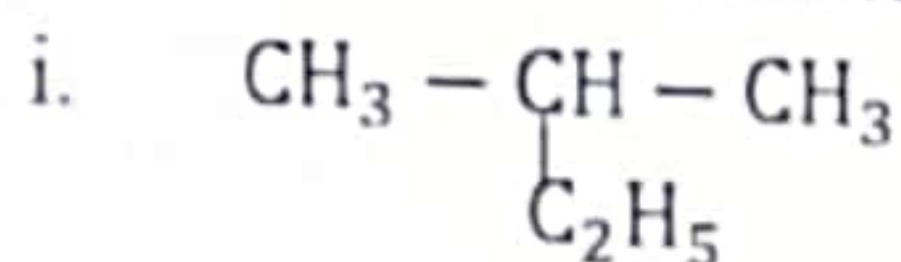
Methane can also be manufactured by subjecting coal to heat and distillation in the absence of air. The process is called **destructive distillation**.

- Together with hydrogen gas, methane is collected in the destructive distillation as **coal gas**. Other products of the distillation, are **coal tar** (the condensable distillate), and **coke** (the residue). Both coal gas and coke are useful fuels.

PRACTICE EXERCISE 10

Problem 1

Give systematic names of the following organic compounds



Problem 2

Draw a structure and give a name of the position isomer of 2-methylpentane.

Problem 3

Name all skeletal isomers of 2, 2-dimethylbutane

Problem 4

Write a chemical equation to show preparation of:

- Ethane from propanoic acid
- Ethane from ethene
- Hexane from bromopropane
- Propane from propyl magnesium iodide
- Propane from chloropropane
- $\text{CH}_3\text{CH}_2\text{CH}_3$ from CH_3COCH_3

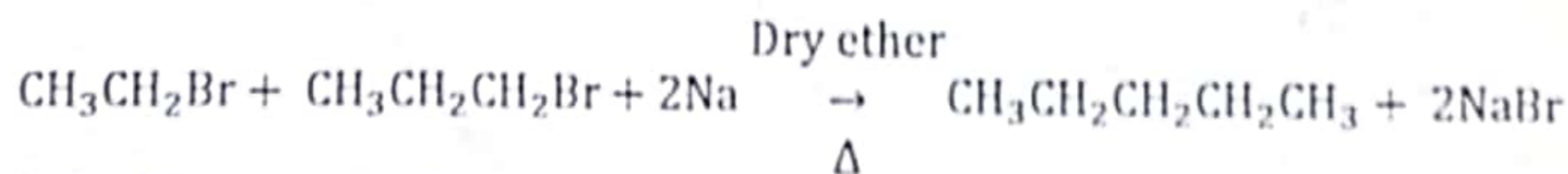
Problem 5

Complete the following organic reactions:

- $\text{Al}_4\text{C}_3 + \text{H}_2\text{O} \xrightarrow{\Delta}$
- $\text{CH}_3\text{CH}_2\text{COONa}(\text{aq}) \xrightarrow{\text{Electrolysis}}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2 \xrightarrow{\text{uv}}$
- $\text{CH}_3\text{CH}_3 + \text{Cl}_2(\text{Excess}) \xrightarrow{\text{uv}}$
- $\text{CH}_3\text{COCH}_3 + \text{NH}_2\text{NH}_2 \xrightarrow{\text{KOH}(\text{aq})}$

Problem 6

Malusi intended to prepare pentane by using Wurtz reaction as per equation:



- What is the Wurtz reaction?
- Why ether solution should not be used in the Wurtz reaction?
- Write equations to show the formation of other two products and hence say if the method for preparation of pentane was correct or not?
- Is the method suitable for preparation of methane? Explain.

Chapter 11 ALKENES

Alkenes are unsaturated hydrocarbons with carbon-carbon double bond ($C = C$) as functional group.

- Aliphatic alkanes with only one $C = C$ have general molecular formula of C_nH_{2n} .

Alkenes with two double bonds are known as **diene**.

- Aliphatic dienes have general molecular formula of C_nH_{2n-2} . Thus aliphatic dienes are functional isomers to aliphatic alkynes (which have only one $C \equiv C$) with equal number of carbons.

Alkenes with three carbon-carbon double bonds are known as **trienes**.

- Aliphatic trienes have general molecular formula of C_nH_{2n-4} .

CLASSIFICATION OF DIENES

Dienes can be classified into the following categories:

- Cumulated dienes
- Conjugated dienes
- Isolated dienes

Cumulated double bond dienes

These are dienes whereby all two double bond share at single carbon, i.e. there is no carbon – carbon single bond between the two double bonds.

- Examples of cumulated double bond dienes are:

- $CH_2 = C = CH_2$
- $CH_3CH = C = CH_2$

Conjugated double bond dienes

These are dienes with only one carbon – carbon single bond separating the two carbon – carbon double bonds.

Examples:

- $CH_2 = CH - CH = CH_2$
- $CH_3CH = CH - CH = CH_2$

Isolated double bond dienes

- These are dienes with more than one carbon – carbon single bonds separating the two carbon – carbon double bonds.

Examples:

- $CH_3CH = CH - CH_2 - CH = CH_2$
- $CH_3CH = CH - CH_2 - CH_2 - CH = CH_2$

SYSTEMATIC NOMENCLATURE OF ALKENES

Rules of naming alkenes are the same as those of naming alkanes with the following modifications:

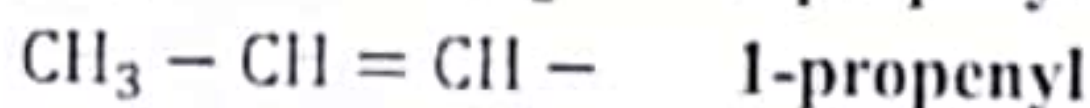
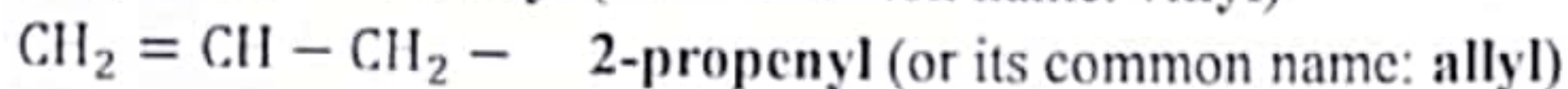
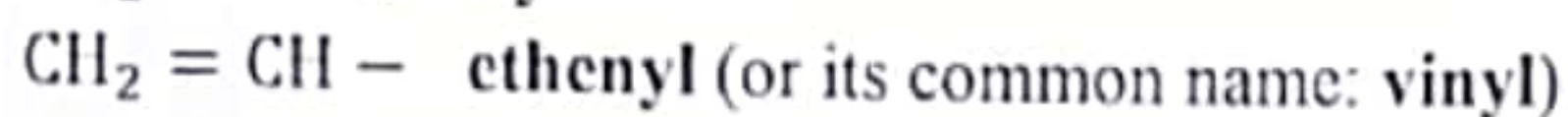
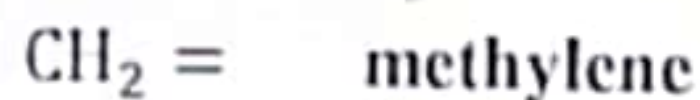
- The parent chain must contain carbon – carbon double bond; i.e. the parent chain is the longest continuous carbon chain of carbon with $C = C$.
- Numbering of carbons in the parent chain starts at the end which is closer to carbon – carbon double bond ($C = C$).

- Position of $C = C$ should be indicated by using Arabic numerals and the position shown must be that of the first carbon with the double bond.
- The parent name should end with suffix **-ene**.

Alkenes as substituents

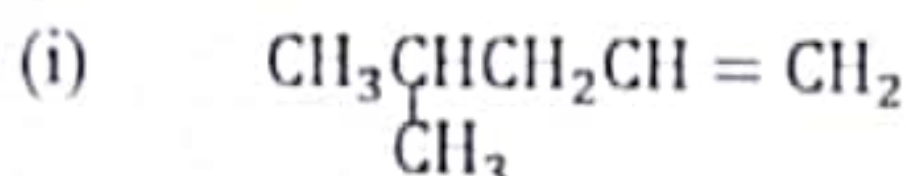
In some cases, a group containing an alkene may need to be treated as a substituent.

- Alkene names as substituents are called **alkenyl groups**. *Alkenyl group is a hydrocarbon group formed when a hydrogen atom is removed from an alkene group.*
- Alkenyl groups may be named either systematically by replacing the **-e** from the parent alkene's name with **-yl** like in alkyl groups or by using common (trivial) names. Below are some common alkenyl groups.

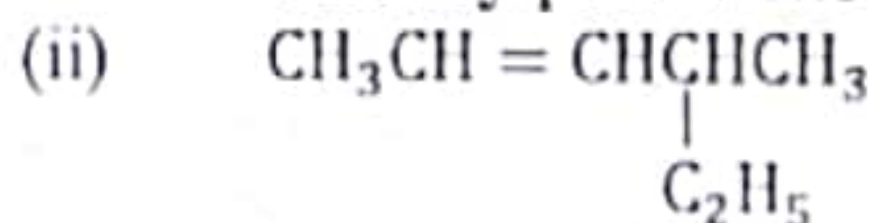


Example 1

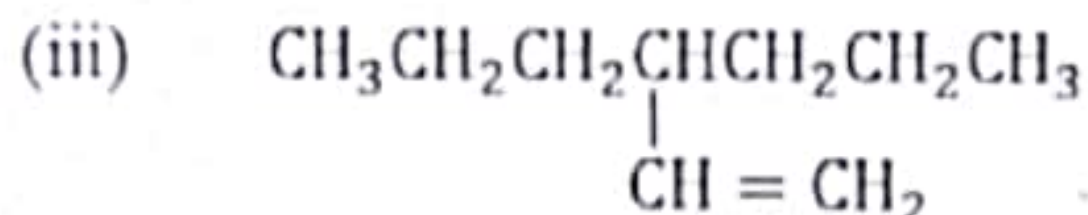
Name the following organic compounds;



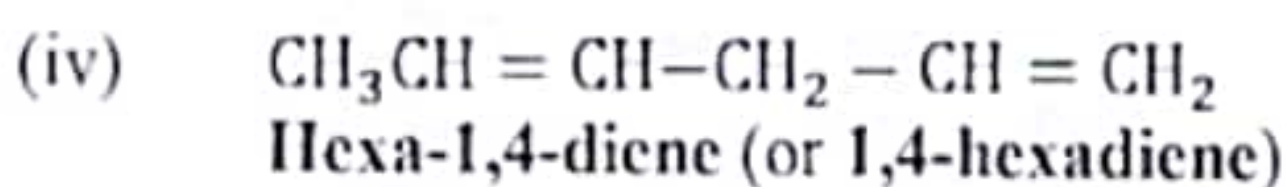
4-methylpent-1-ene (or 4-methyl-1-pentene)



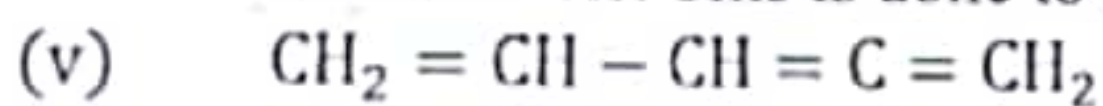
4-methylhex-2-ene



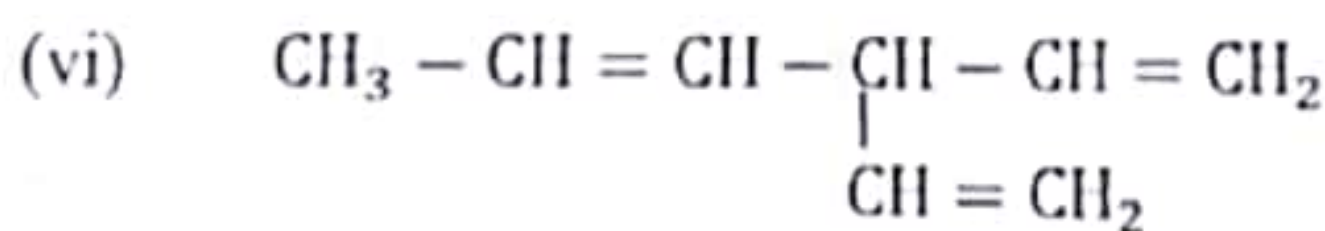
3-propylhex-1-ene (NOT 4-vinylheptane)



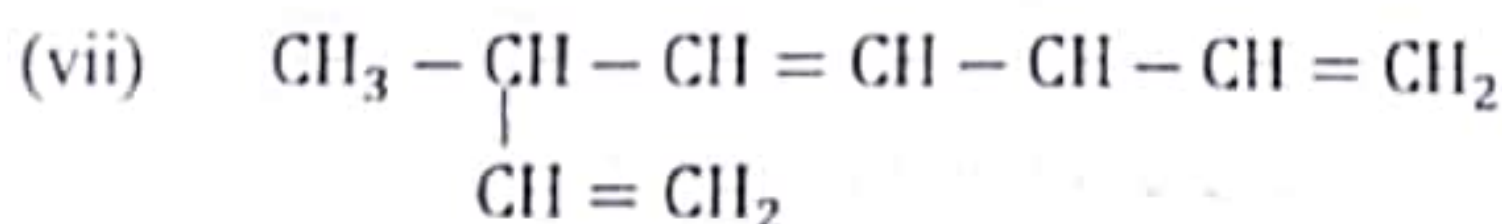
Note: In this case the vowel 'a' has been retained. This is general rule that whenever the ending includes the numerical prefix which begins with consonant (in this case 'd' of 'diene') the vowel of the parent name must be retained, e.g. propadiene instead of propdiene or butatriene instead of buttriene etc. This is done to make pronunciation easier.



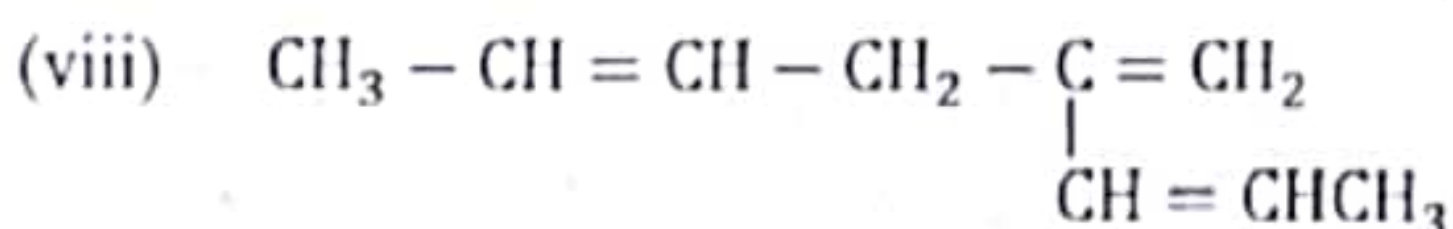
Penta-1,2,4-triene (Again notice the inclusion of the vowel 'a' and don't forget to apply lowest sum rule for numbers representing position of $C = C$)



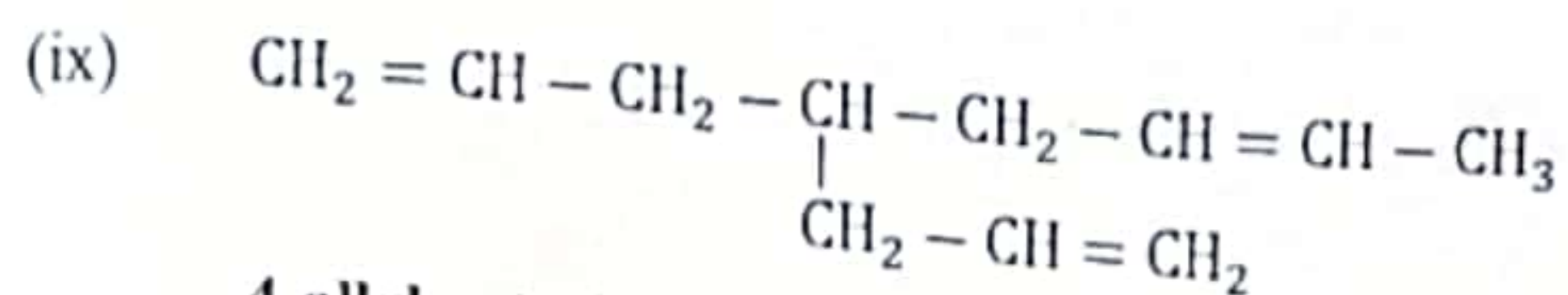
3-vinylhexa-1,4-diene (or 3-ethenylhexa-1,4-diene)



3-methylocta-1,4,7-triene (NOT 6-methylocta-1,4,7-triene. NOT 6-vinylhepta-1,4-diene)



4-methyleneocta-2,6-diene



4-allyl-octa-1,6-diene or 4-(2-propenyl)octa-1,6-diene

It should be noted that:

As common (trivial or commercial) names, alkenes are named as alkylene. For example ethylene for ethene, propylene for propene or butylenes for butane.

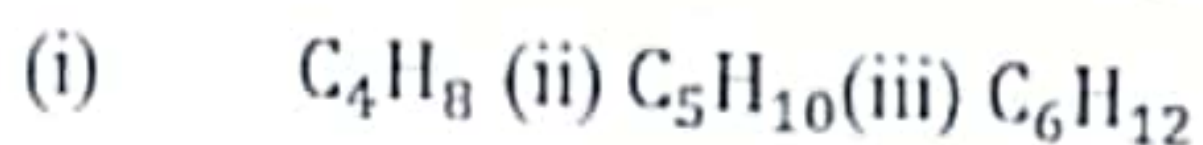
ISOMERISM IN ALKENES

Aliphatic alkenes can exhibit the following types of isomerism:

- Skeletal /chain isomerism
- Position isomerism
- Functional isomerism (for aliphatic diene)
- Geometric isomerism.

Question

Write structures and names of all possible isomers of a compound with molecular formula of:

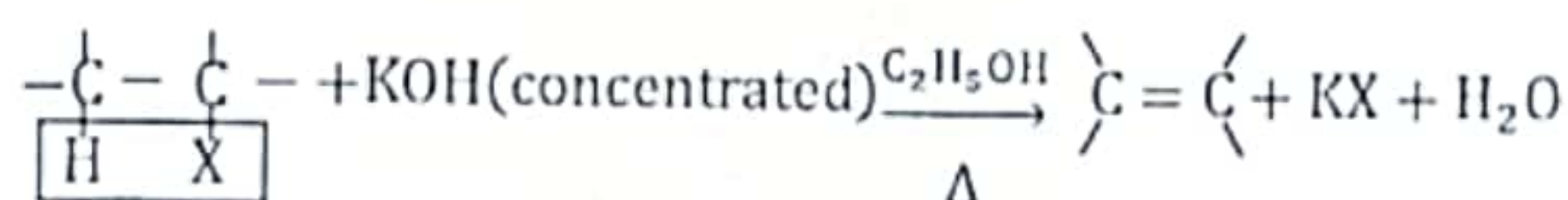


PREPARATIONS OF ALKENES

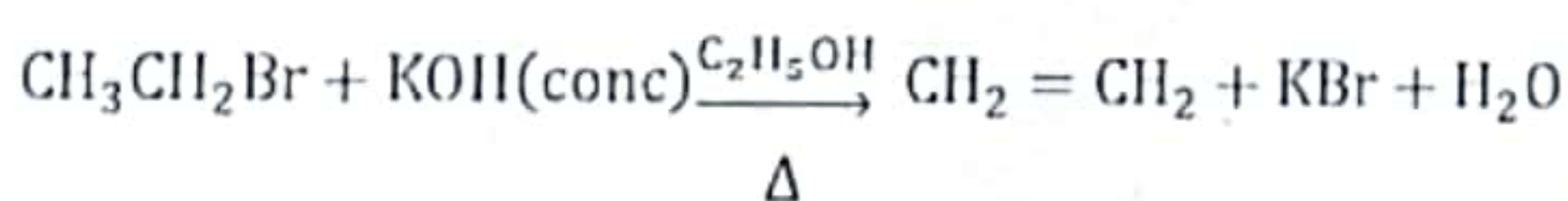
Dehalohydrogenation of haloalkane

When haloalkane is heated with alcoholic strong alkaline solution like KOH, alkene is formed.

Generally:



Example:

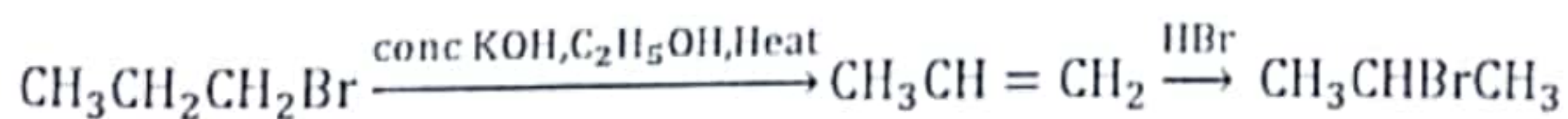


The above reaction is very important in converting primary haloalkane into secondary haloalkane.

Example 2

Convert $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ into $\text{CH}_3\text{CHBrCH}_3$

Solution



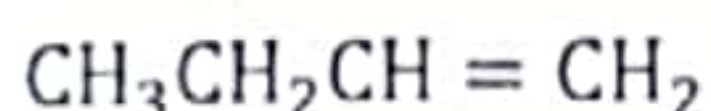
The reader should understand that:

Elimination reaction to form alkene is governed by Saytzeff's rule which states that:

Alkene with greater number of alkyl groups at double bond is more stable.

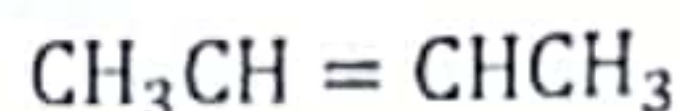
Thus according to the rule; if there is possibility of forming more than one alkene in the elimination reaction, the major product is the alkene with greater number of alkyl groups at the double bond.

- For example, elimination reaction of 2-chlorobutane may give but-1-ene or but-2-ene.



but-1-ene

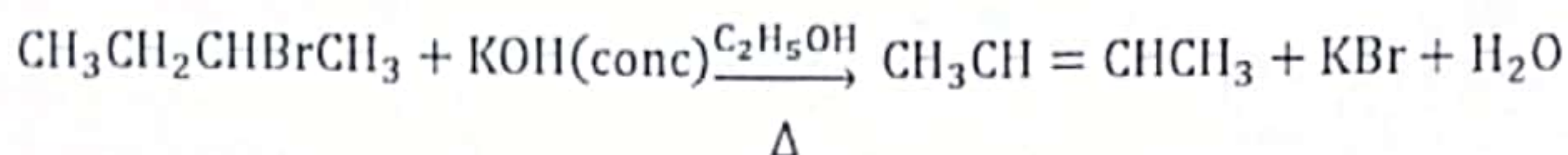
(has only one alkyl, i.e. ethyl group at the double bond)



but-2-ene

(has two alkyl, i.e. methyl groups at the double bond)

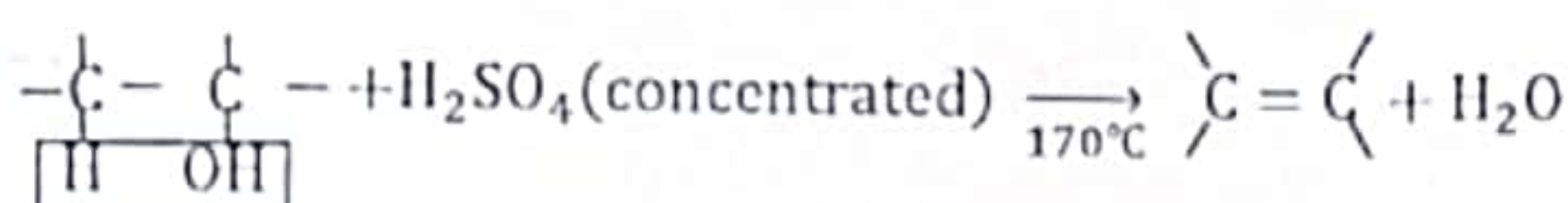
Therefore but-2-ene having greater number of alkyl groups at the double bond becomes the major product.



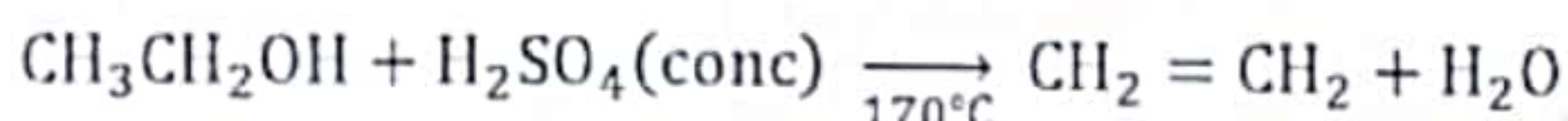
Dehydration of alcohols

When alcohol is heated with concentrated sulphuric acid to temperature of about 170°C, elements of water are eliminated from adjacent carbon atoms resulting to formation of alkene.

Generally:



Example:

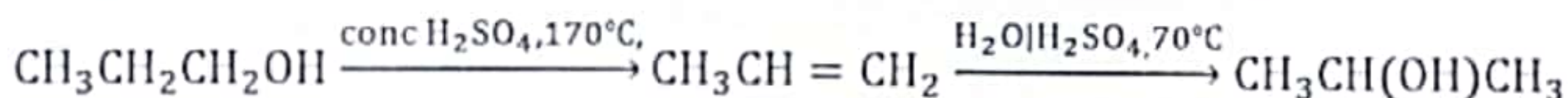


The above reaction is very important in converting primary alcohol into secondary alcohol.

Example 3

Convert $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ into $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

Solution



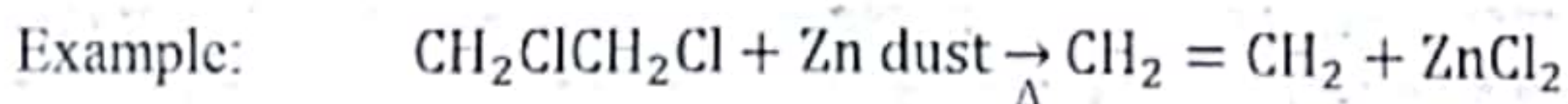
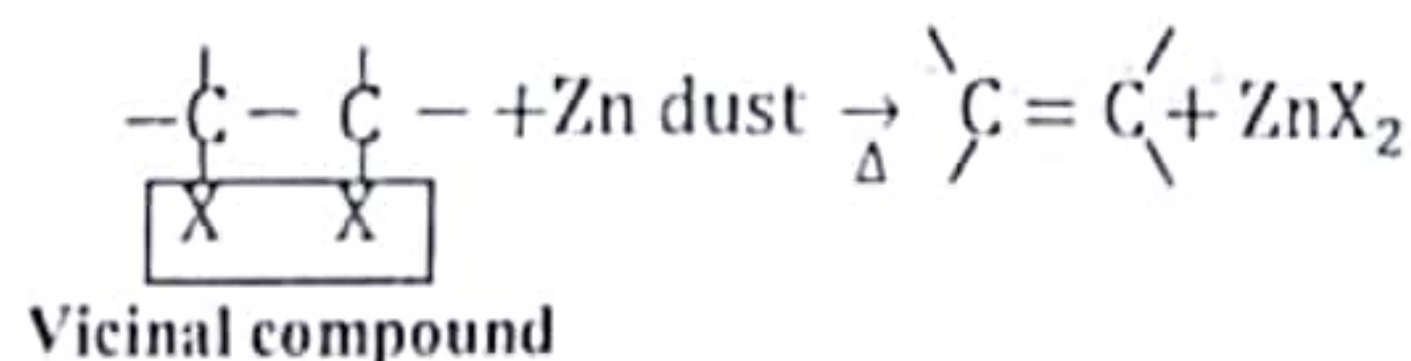
It should be noted that:

Other dehydrating agent like Al_2O_3 , anhydrous ZnCl_2 and concentrated H_3PO_4 may be used to dehydrate alcohol thus forming alkene.

Dehalogenation of vicinal compounds

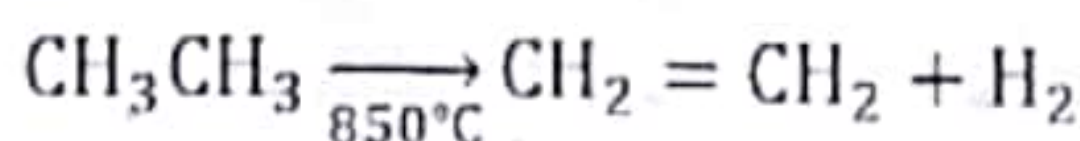
When vicinal compound is heated with zinc dust, alkene is formed. Vicinal compound is the dihaloalkane with the two halogens at adjacent carbon atoms.

Generally;



Dehydrogenation of ethane

When ethane is heated to temperature of about 850°C, two hydrogen atoms are eliminated from adjacent carbon atoms resulting to formation of ethene.



It should be understood that:

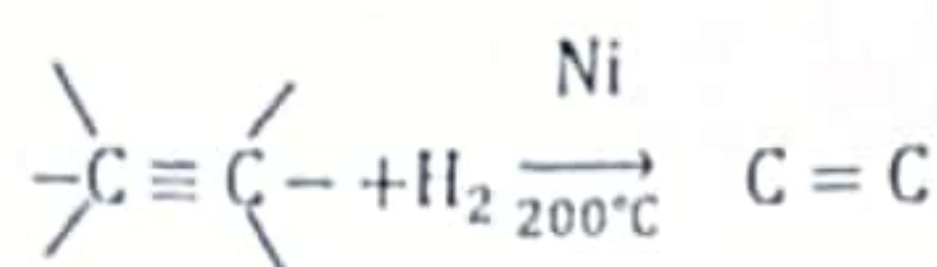
Ethene (of course and propene) can also be produced industrially by cracking reaction explained in the chapter 10.

Controlled hydrogenation of alkyne

When alkyne is carefully heated with limited amount of hydrogen under presence of nickel, platinum or palladium catalyst, alkene is formed.

- The hydrogenation must be carefully controlled to avoid further hydrogenation of alkene to alkane.

For example;



To ensure greater percentage yield of alkene, the **poisoned catalyst** (one that is partly deactivated) is commonly used for the hydrogenation.

- Palladium that has been treated with **quinoline** or **barium sulphate** is a typical poisoned catalyst used for this purpose.

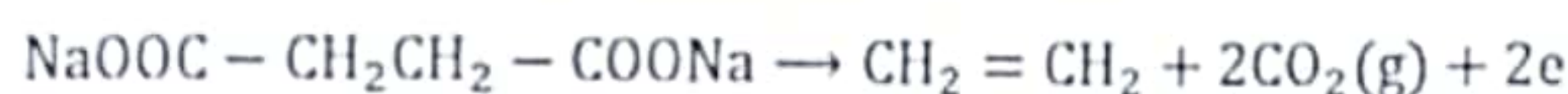


Kolbe's electrolytic method

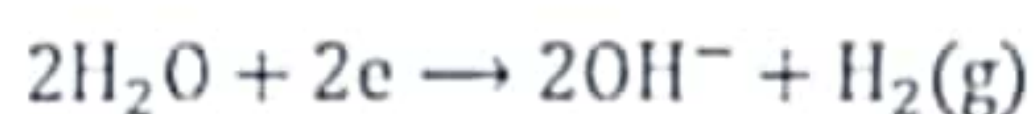
When an aqueous solution of sodium or potassium salt of a dicarbox acid is electrolysed, an alkene is produced.

- For example, electrolysis of sodium butanedioate (commonly known as sodium succinate) gives ethene.

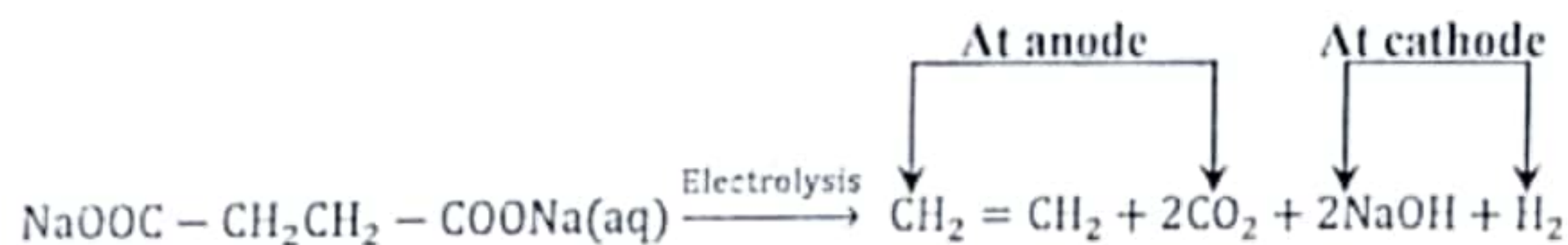
At anode:



At cathode:



Hence the overall reaction equation becomes:



CHEMICAL REACTIONS OF ALKENES

In comparison to alkanes, alkenes are more reactive as result of presence of π -bond in its functional group ($\text{C}=\text{C}$). Presence $\text{C}=\text{C}$, one of which is π (pi) and another is σ (sigma) means the unstable π bond can be broken easily leaving the stable σ bond holding the molecule.

- Alkenes have unsaturated nature and therefore most of their reactions are electrophilic **addition** reactions involving cleavage of the π bond followed by addition of atoms to carbons originally with the π bond.

Electrophilic addition reactions in alkenes are governed by **Markownikoff's** (also spelled as **Markovnikov's**) rule of electrophilic addition which state that:

When unsymmetrical molecule is added to unsymmetrical alkene, an electrophile tends to add to carbon which has directly bonded to greater number of hydrogen atoms.

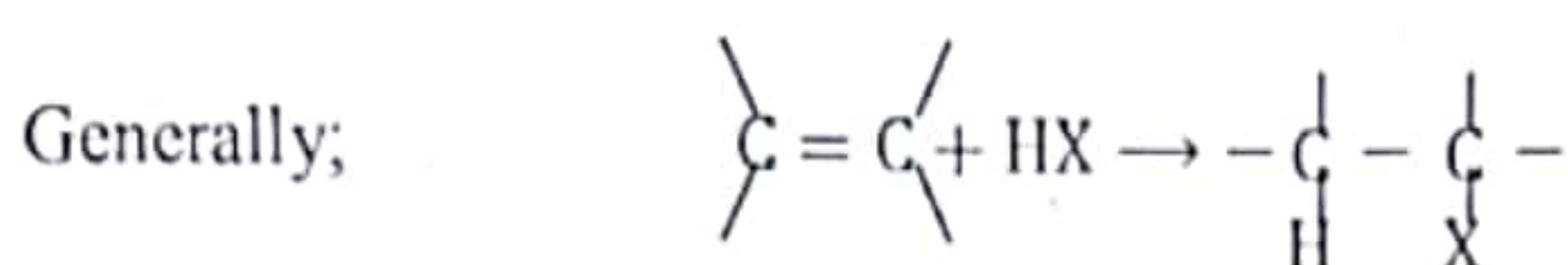
Markownikoff's rule is justified by stability of intermediate carbenium ion of the reaction mechanism, i.e. electrophilic addition product obtained according to Markownikoff's rule is favoured by higher stability of intermediate carbenium ion which is brought about by stronger positive inductive effect as explained earlier in the chapter 6.

- Below are examples of chemical reactions of alkenes.

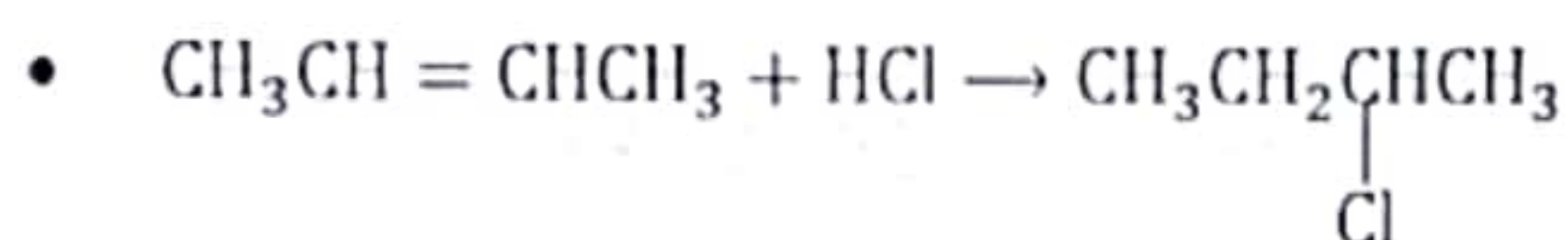
Halohydrogenation

Alkenes react with gaseous hydrogen halide resulting to formation of haloalkane. You should notice the use of the word 'gaseous'; *why solution of hydrogen halide should not be used?*

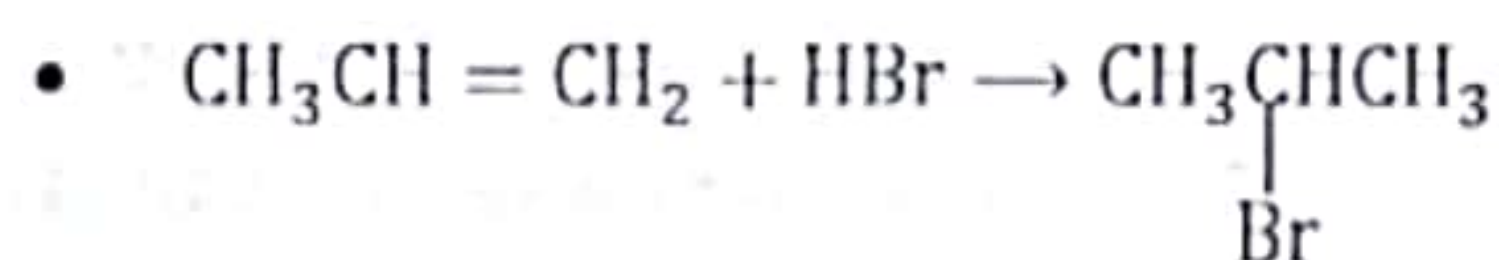
- This is simply because the use of solution of hydrogen halide yields mixture of products as water in the solution can also add to the $C = C$.



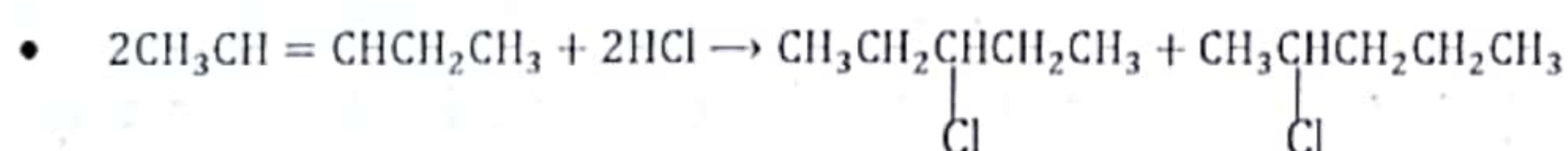
Examples:



In this example, alkene is symmetrical. That means there is a possibility of forming one product only and hence there is no need for application of Markownikoff's rule.



Here the alkene is unsymmetrical, so Markownikoff's rule should be applied by H which is electrophile adding to the carbon with greater number of hydrogen atoms, i.e. the carbon with CH_2 .



Interesting...! In this example, alkene is unsymmetrical. That may suggest we should apply Markownikoff's rule. However with single hydrogen in each, there is an equal number of hydrogen atoms to carbons with double bond. So to understand the product formation, we must go back to the stability of intermediate carbenium ion by considering all two possibilities of forming the products (You should be able to do this on your own). You will find that the two carbenium ions have equal stability and hence all two products have equal possibility of existing. As a rule, **whenever the unsymmetrical alkene has equal number of hydrogen atoms at carbons with double bond, write all possible products.**

The reader should understand that:

Under presence of organic peroxide, hydrogen bromide undergo anti-Markownikoff's addition, i.e. *When HBr is added to unsymmetrical alkene under presence of organic peroxide, hydrogen tends to add to carbon with fewer hydrogen atoms (Anti-Markownikoff's rule).*

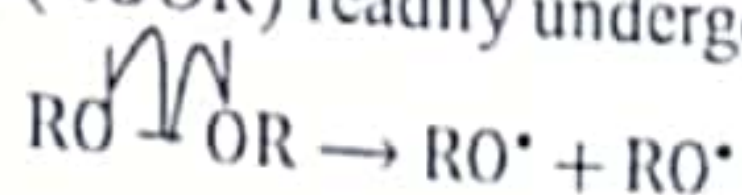
- To understand this considers mechanism of addition of HBr to prop-1-ene.

Under presence of organic peroxide the reaction is not electrophilic addition reaction but is free radical addition reaction (Presence organic peroxide favour homolytic bond cleavage which results to formation of free radicals).

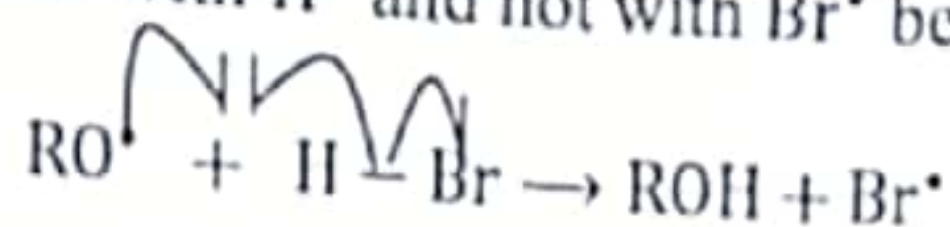
- The reaction takes place through the following steps:

First step: Formation Br•

Under organic peroxide (ROOR) readily undergoes homolytic bond cleavage, to form free radical.

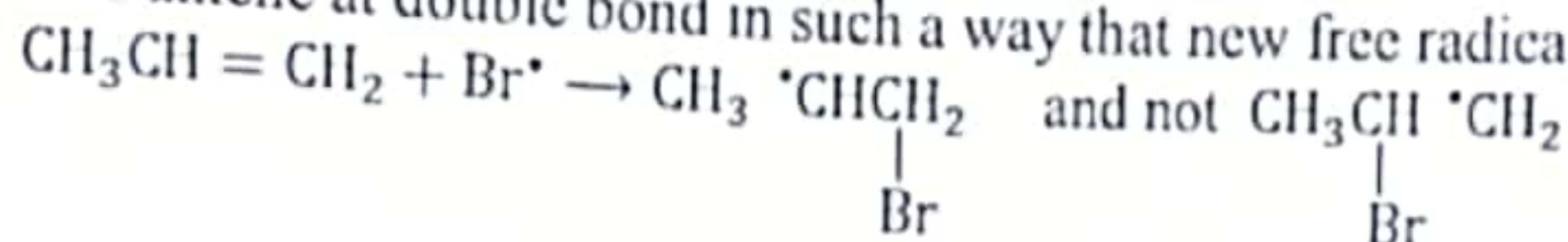


RO• formed activate homolytic bond cleavage of HBr by combining with H• from HBr yielding ROH and Br•. RO• combines with H• and not with Br• because H• is more reactive than Br•.



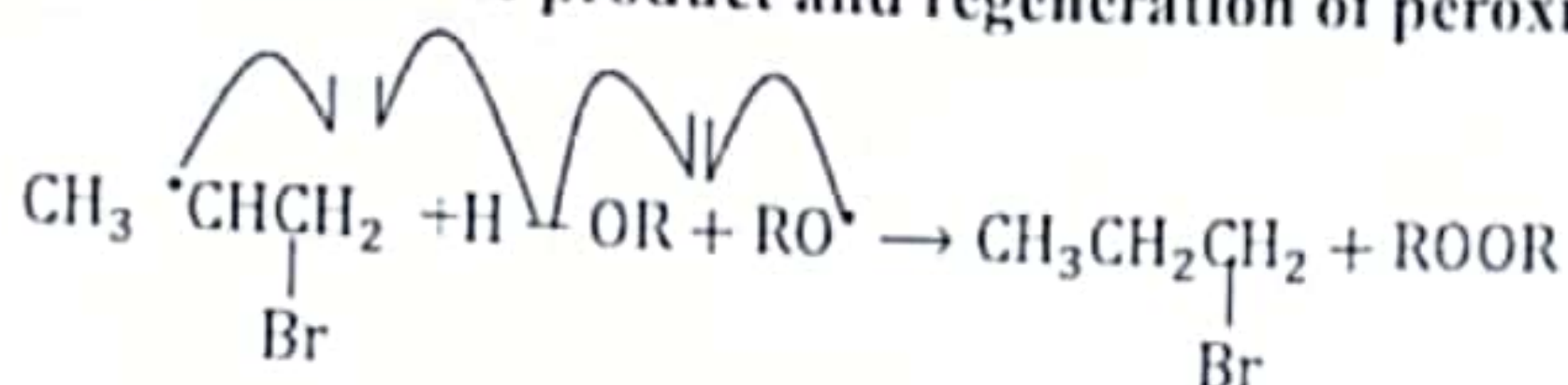
Second step: Addition of Br• to alkene

Br• attacks alkene at double bond in such a way that new free radical which is formed is more stable.



2° free radical, more stable 1° free radical, less stable

Third step: Formation of product and regeneration of peroxide



Hence overall reaction equation becomes: $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{ROOR}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

Why hydrogen chloride and hydrogen iodide do not undergo anti-markownikoff's addition reaction?

Hydrogen chloride and hydrogen iodide do not undergo free radical addition reaction to alkene and therefore they do not undergo anti-Markownikoff's addition reaction. This is due to the following reasons:

- Homolytic bond cleavage of HCl to form free radicals is very slow due to greater stability of H – Cl bond thus making difficulty for bond to break homolytically.
- I• is very unreactive such that its addition to alkenes is endothermic and too slow to sustain chain reaction despite the fact that H – I bond is weak.

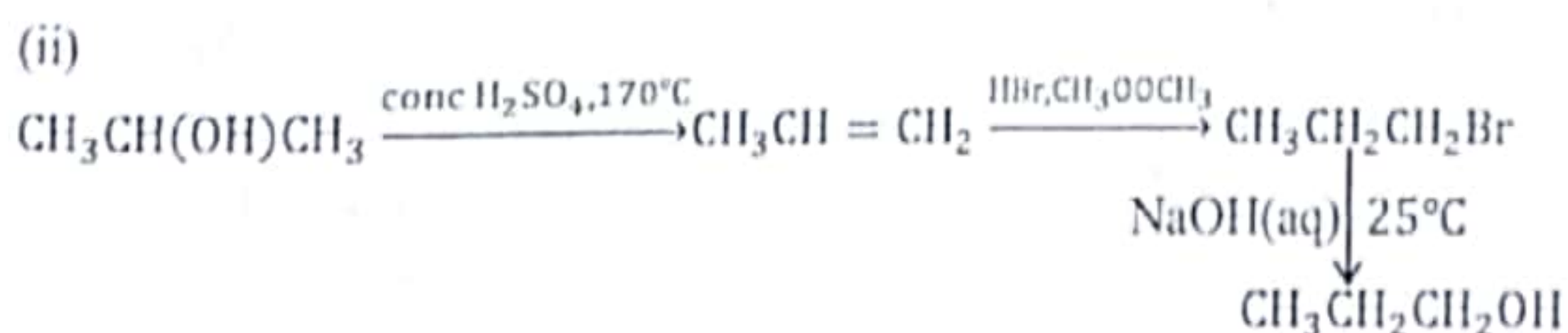
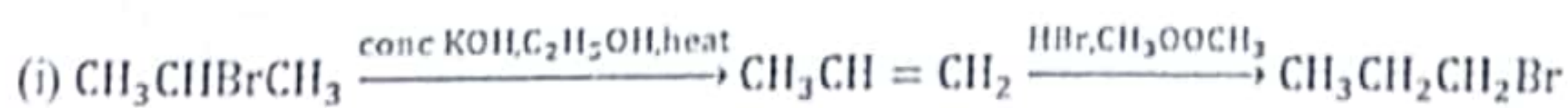
The anti-Markownikoff's addition reaction is very important in converting secondary haloalkanes or alcohol into primary haloalkanes or alcohols.

Example 4

How would you convert:

- $\text{CH}_3\text{CHBrCH}_3$ into $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ into $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Solution



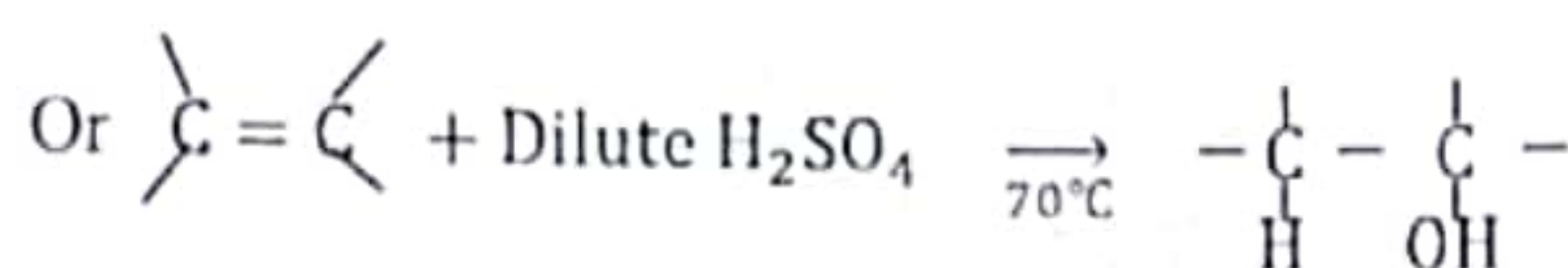
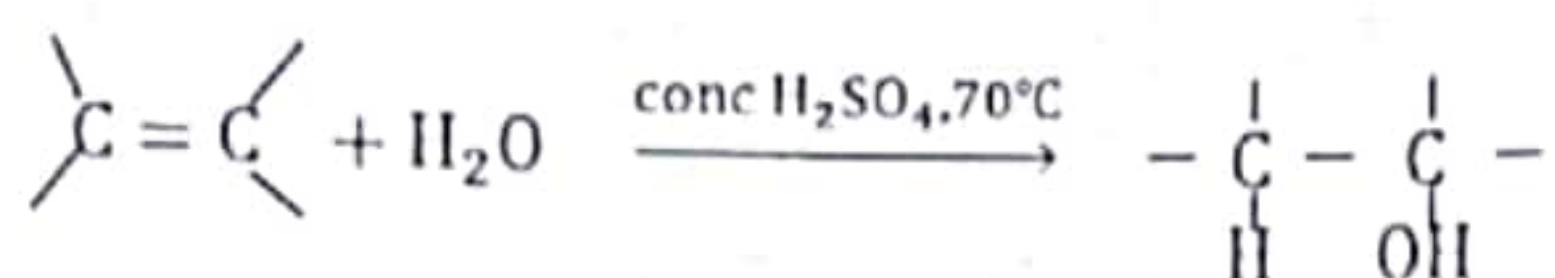
Don't forget that:

Presence or absence of hydrogen peroxide has no effect when hydrogen chloride and hydrogen iodide is employed; i.e. whether in presence or absence of hydrogen peroxide, alkenes tend to undergo Markownikoff's addition reactions when either HI or HCl is added.

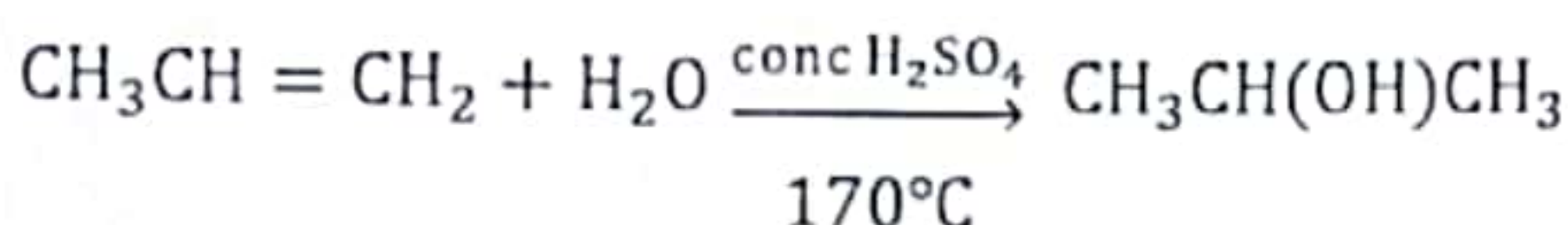
Reaction with hot water under presence of sulphuric acid

Under presence of sulphuric acid alkene react with water heated to temperature of about 70°C resulting to formation of alcohol. The reaction is also known as **hydration of alkene**.

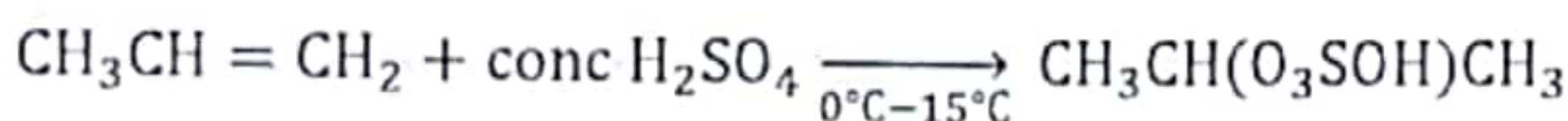
Generally;



Example:

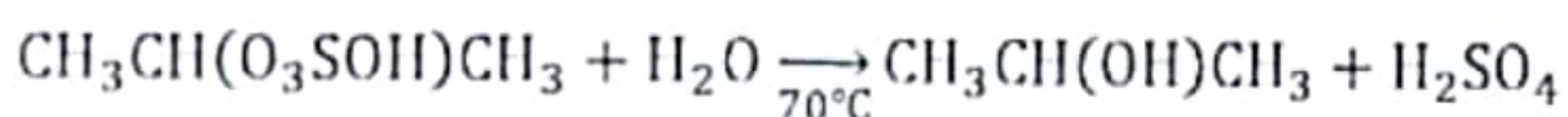


But:



White precipitate

When the above product is mixed with hot water heated to temperature of about 170°C alcohol is formed.



Therefore, in the hydration reaction of alkene, sulphuric acid is used as catalyst.

The reader should understand that:

Formation of white precipitate when alkene is allowed to react with cold concentrated sulphuric acid is a test of unsaturation.

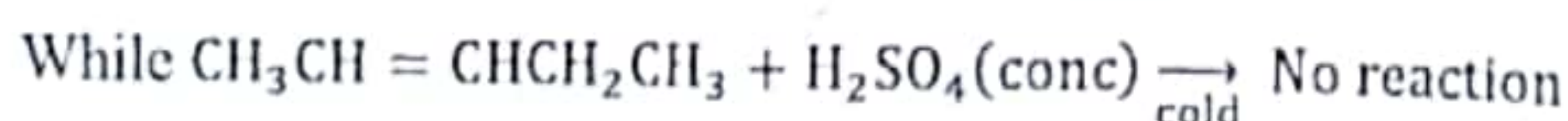
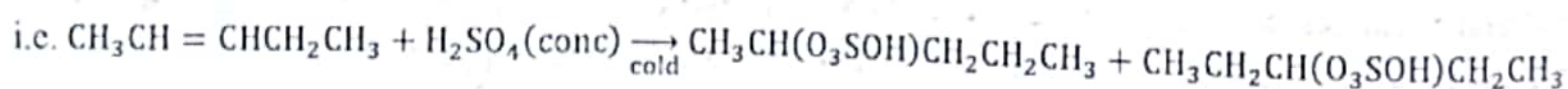
- Also since the white precipitate can be converted into alcohol which in turn can be converted back into alkene by dehydration, the reaction is very important in separating mixture of alkene and alkane.

Example 5

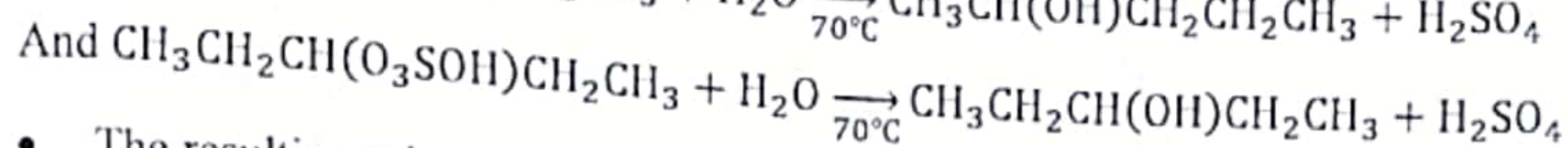
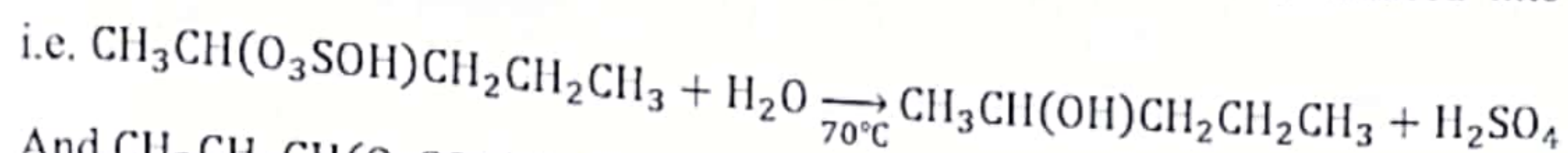
Without considering their boiling point, explain how you will get pure pent-2-ene and hexane from their mixture i.e. from mixture of pent-2-ene and hexane.

Solution

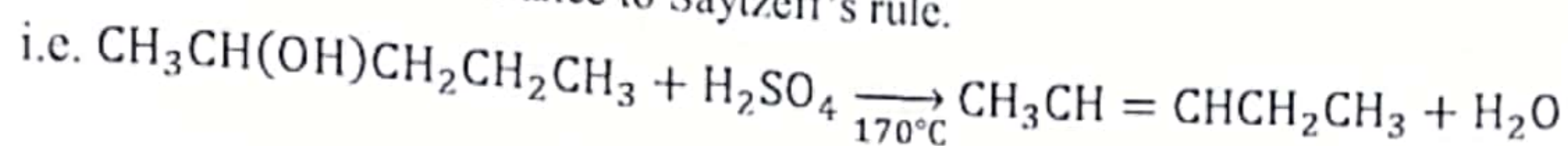
- Cold concentrated Sulphuric acid is introduced in the mixture.
- Pent-2-ene being unsaturated hydrocarbon gives white precipitate with the sulphuric acid while hexane being saturated hydrocarbon does not.



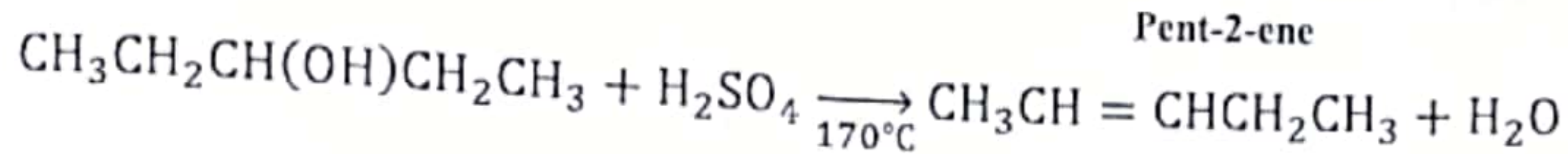
- The resulting mixture obtained after introduction of cold concentrated sulphuric acid is then filtered to get filtrate and residue.
- The **filtrate is pure hexane** and the residue is mixture of $\text{CH}_3\text{CH}(\text{O}_3\text{SOH})\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{O}_3\text{SOH})\text{CH}_2\text{CH}_3$.
- Thereafter water heated to temperature of about 70°C is introduced into the residue to form alcohols.



- The resulting mixture is then heated to temperature of about 170°C and in both cases **pent -2-ene** is obtained in accordance to Saytzeff's rule.



Pent-2-ene

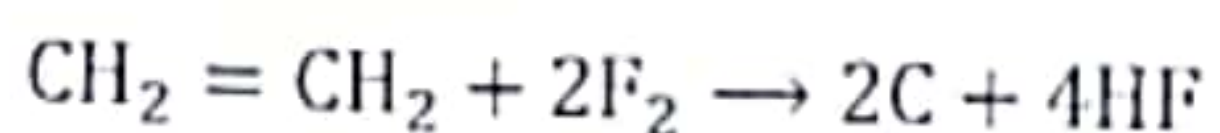


Pent-2-ene

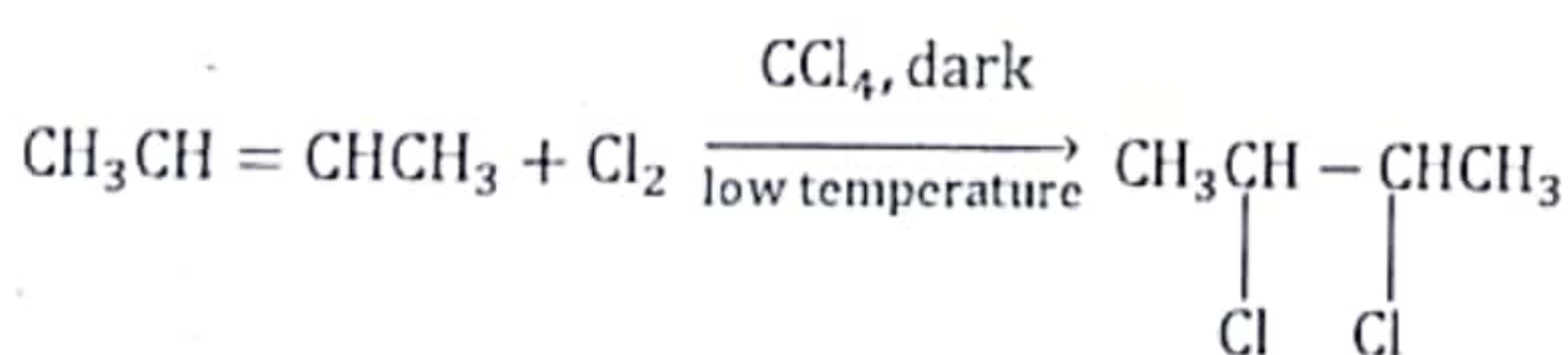
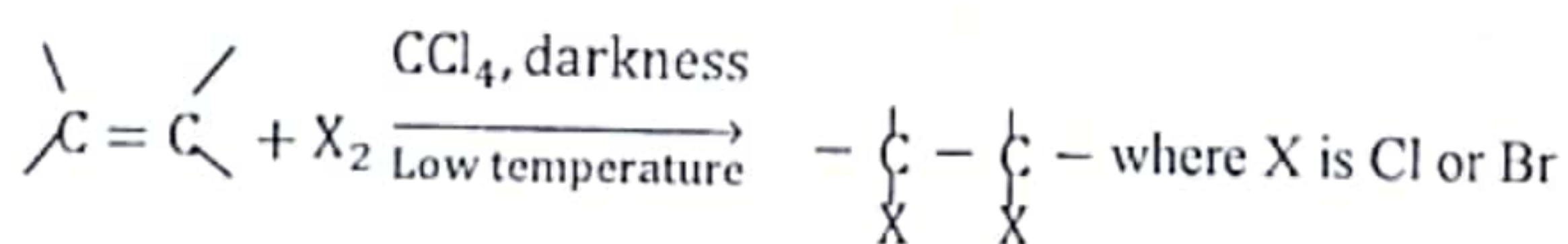
Halogenation

Alkenes react with halogens in darkness and low temperature under presence of organic solvent like CCl_4 or CH_2Cl_2 to form dihaloalkanes.

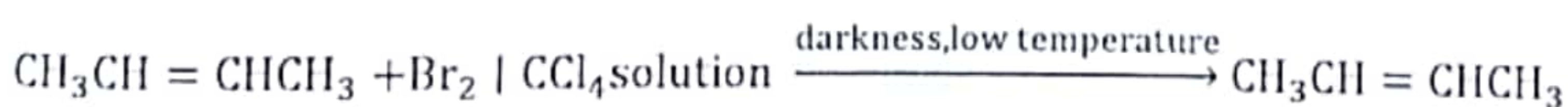
- Only Cl_2 and Br_2 are useful for this purpose.
- F_2 is not useful because undergoes explosive reaction with alkene to give carbon and hydrogen fluoride while iodine is unreactive having almost no reaction with alkenes.



Generally;



When bromine is used, its reddish brown colouration gets decolourised and therefore the reaction can be used as a test of unsaturation.

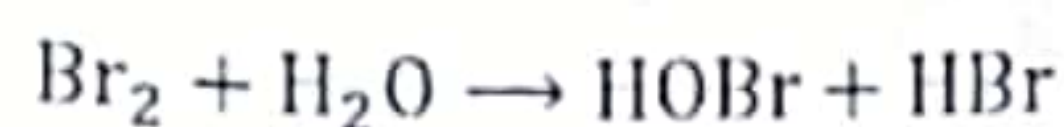


Attention!

Also alkane can decolourise bromine but UV light or very high temperature must be present for this to happen. So the difference between alkane and alkene in this case is that; while alkenes can decolourise bromine in absence of UV light or very high temperature, i.e. in darkness and low temperature alkanes can not. Most students make a mistake by saying 'Alkene decolourise reddish brown colouration of bromine while alkane does not' without mentioning; '**under darkness and low temperature, alkene.....while alkane.....**'

Reaction with bromine water

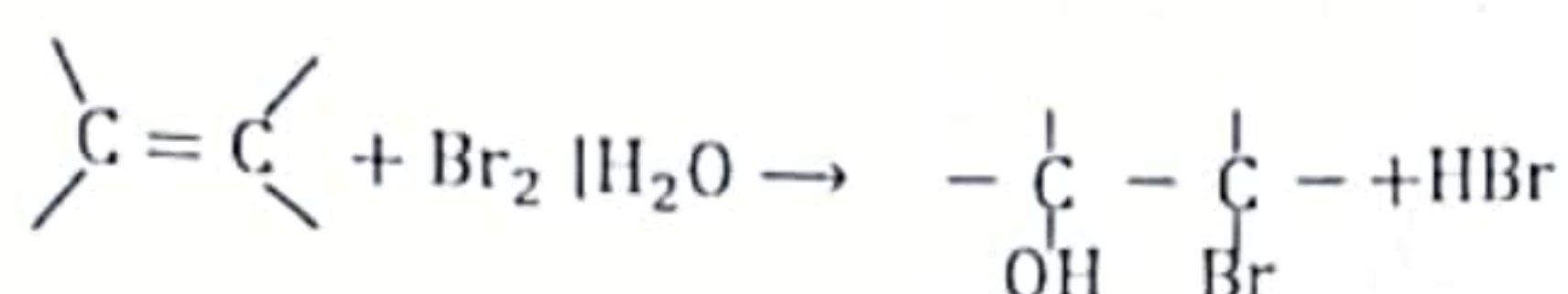
Bromine water is reacting mixture of bromine and water.



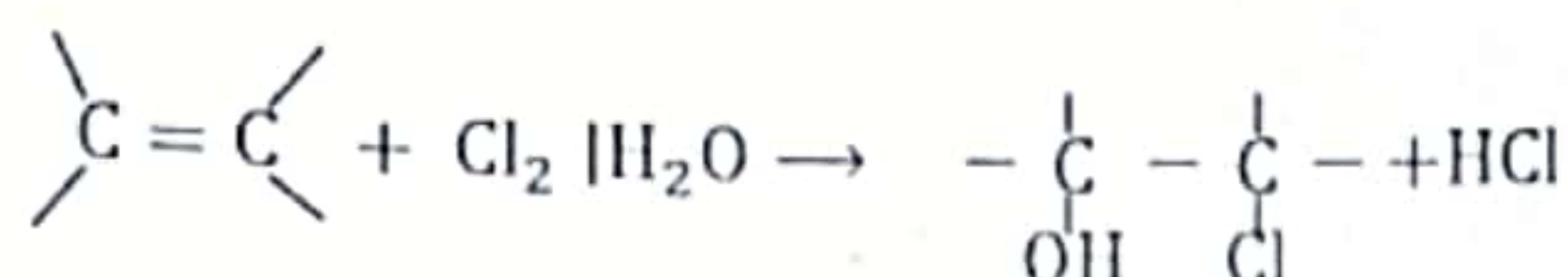
When alkene is mixed with, a 1,2-bromohydrin (a compound with a Br and OH on adjacent carbon atoms) is formed.

- The reaction involves decolourisation of reddish brown colouration of bromine and therefore it is another test of unsaturation. The test is known as **bromine water test**.

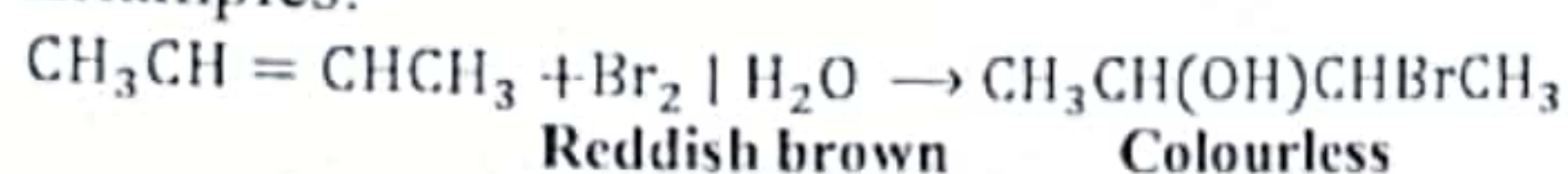
Generally;



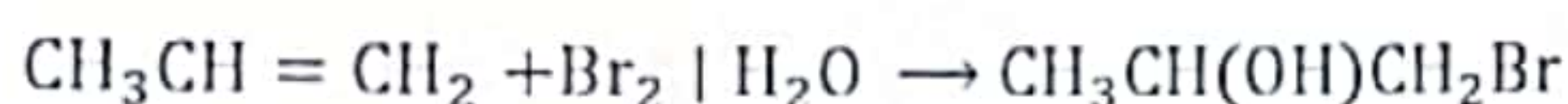
Similarly;



Examples:



Here the alkene is symmetrical and therefore no need of the application of Markownikoff's rule.

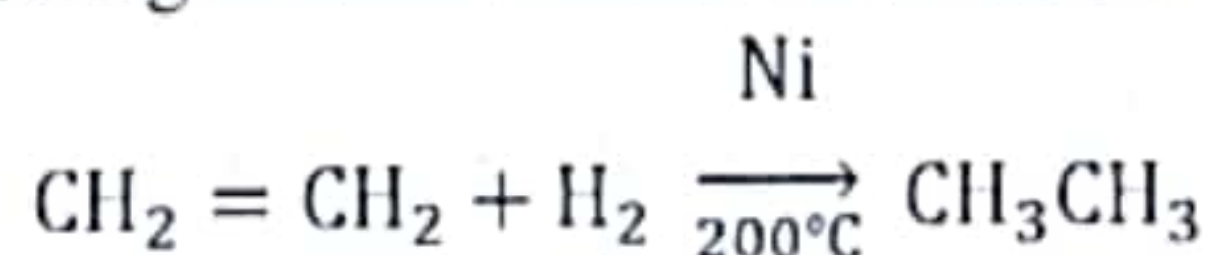


Here the alkene is unsymmetrical and therefore Br must add to the carbon with greater number of hydrogen atoms as electrophile in accordance to Markownikoff's addition.

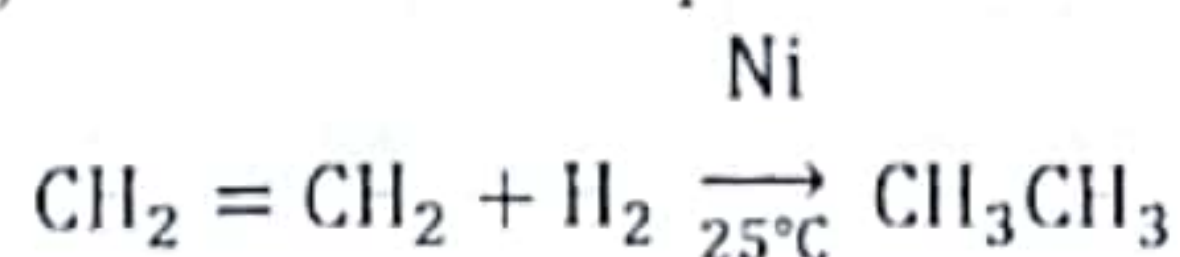
Hydrogenation

Alkenes undergo catalytic hydrogenation to give alkane. Nickel, platinum or palladium catalyst may be used. The reaction is **catalytic reduction** and not electrophilic addition.

- If nickel catalyst is used, the reacting mixture should be heated to temperature of about 200°C.

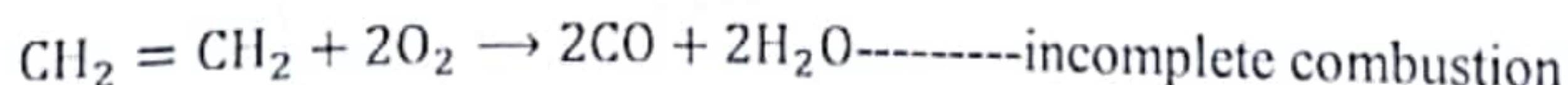
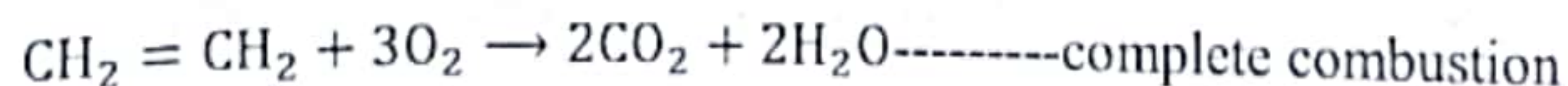


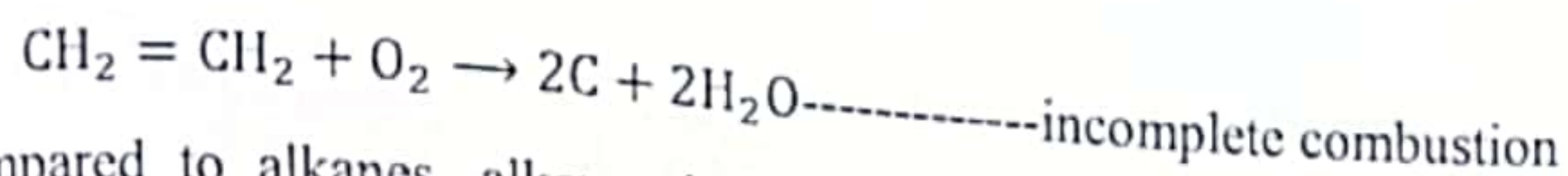
- If platinum or palladium is used, the reaction takes place at room temperature.

**Combustion**

Like alkanes, alkenes can burn in air to give along with water, CO₂ on complete combustion or CO (or C as soot) on incomplete combustion.

For example:





Compared to alkanes, alkenes have lower H:C ratio and therefore are more likely to undergo incomplete combustion.

- Low ability to undergo complete combustion is the one of reasons why alkenes are not commonly used as fuel.
- Another reason is that, alkenes being more reactive (as compared to alkanes) are very useful in synthesizing many important organic compounds.

Oxidation

Alkenes can be oxidised to different products depending on alkene structure and on the reagent used.

- Depending on the way carbon-carbon double breaks, reactions involving oxidation of alkenes can be classified into the following main categories:

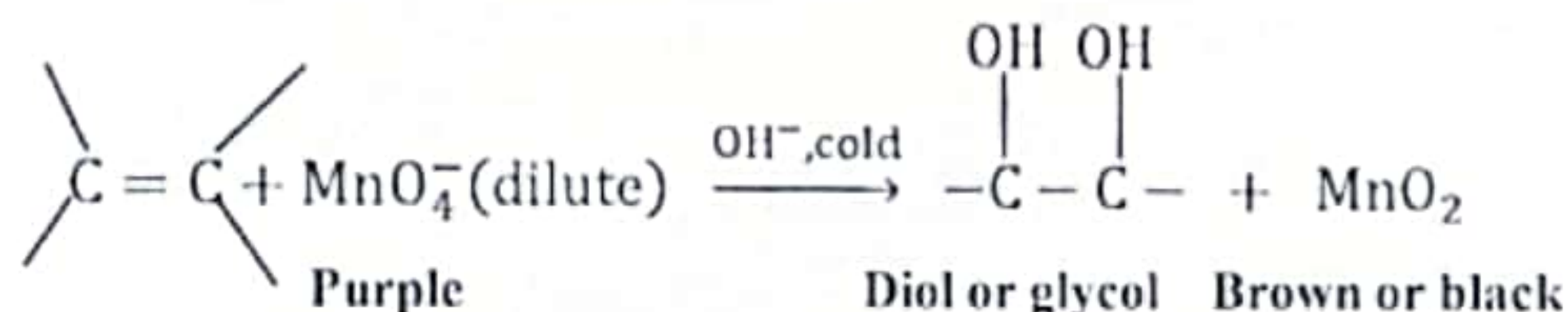
- Oxidation without cleavage of the sigma bond
- Oxidation with cleavage of the sigma bond

Oxidation without cleavage of the sigma bond

The oxidation of the pi bond without cleavage of the sigma bond of $\text{C} = \text{C}$ occurs in the mild oxidation. Important reaction to consider here is **diol (or glycol) formation**.

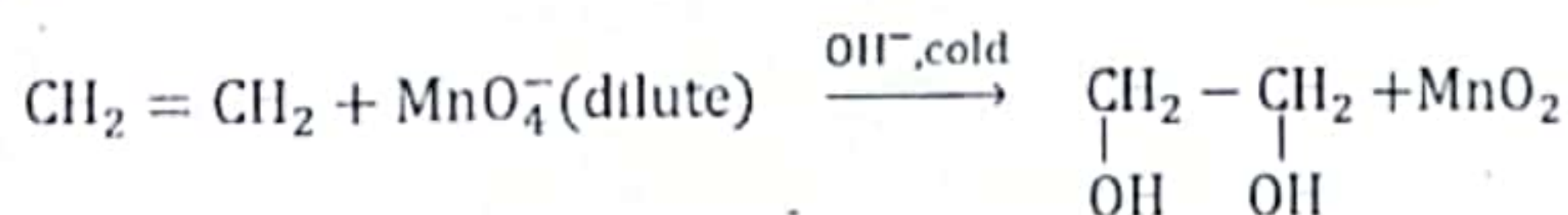
- In the alkaline medium, potassium permanganate (KMnO_4) is weak oxidizing agent. So to ensure mild oxidation of alkene to diol, cold dilute solution of alkaline potassium permanganate is used.

Generally;



The disappearance of purple colouration of potassium permanganate accompanied with formation of brown/black colouration of manganese (IV) oxide is another test of unsaturation. The test is known as **Baeyer test**.

Example:

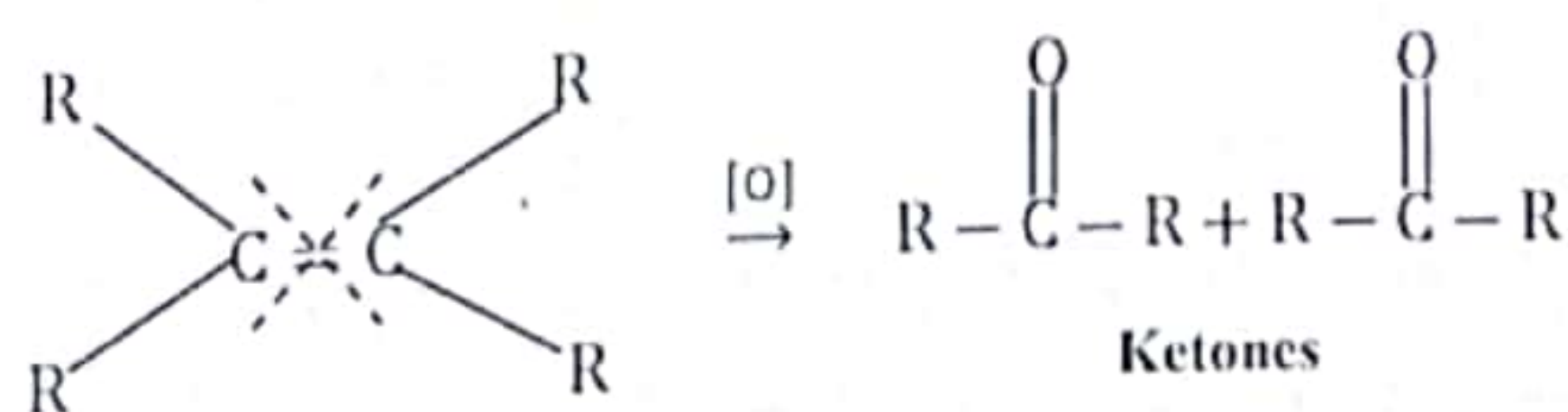


Oxidation with cleavage of the sigma bond

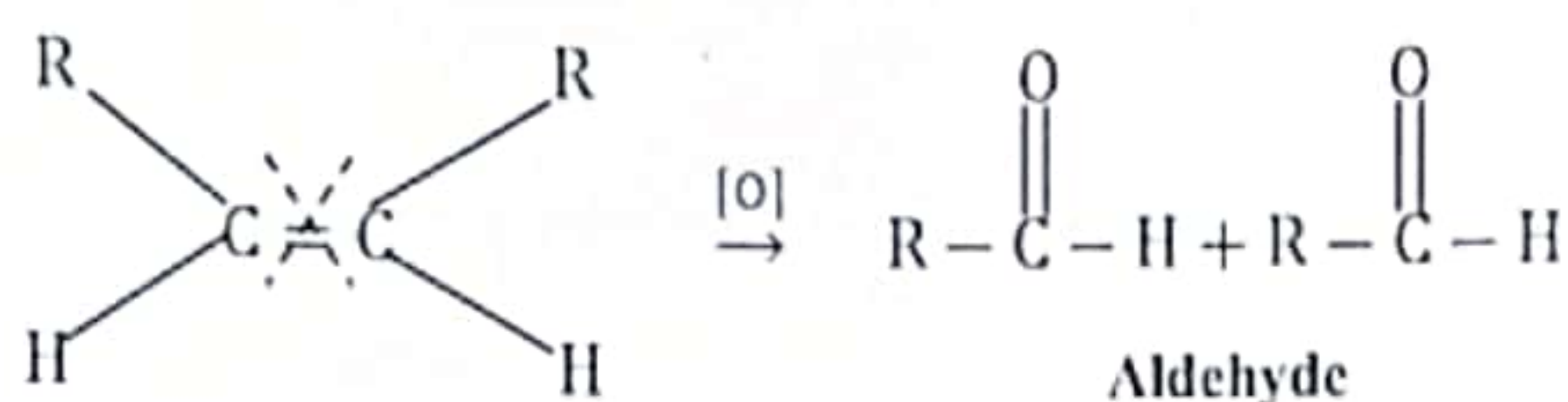
The oxidation of the pi bond with cleavage of the sigma bond of $\text{C} = \text{C}$ occurs in the vigorous oxidation.

- Its products depend upon the oxidizing conditions and upon the structure of the alkene.

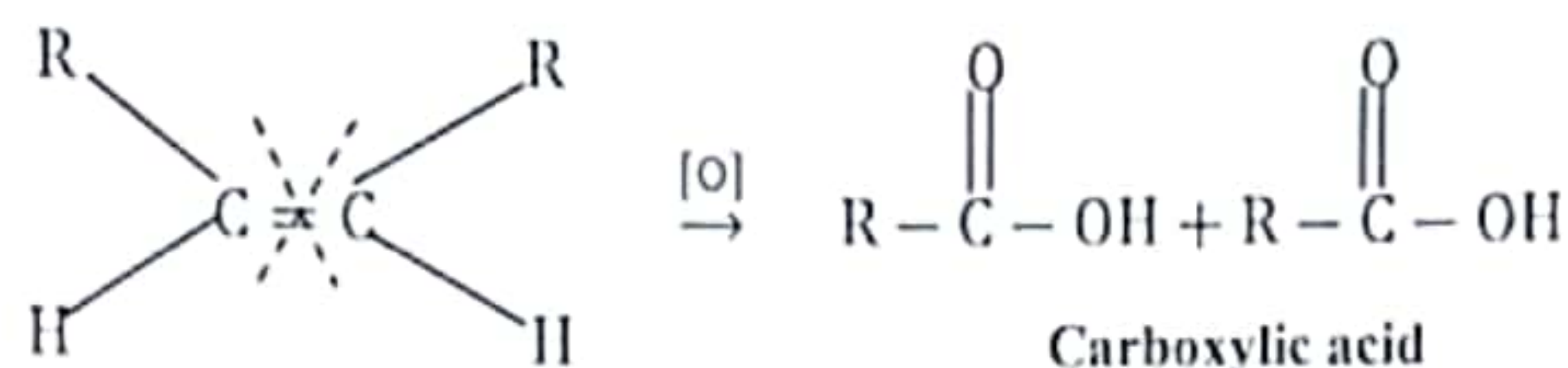
If neither of the alkene carbon (carbon with $\text{C} = \text{C}$) is bonded to hydrogen atom (that is, each double bonded carbon is bonded to two alkyl groups), a pair of ketones molecules is formed.



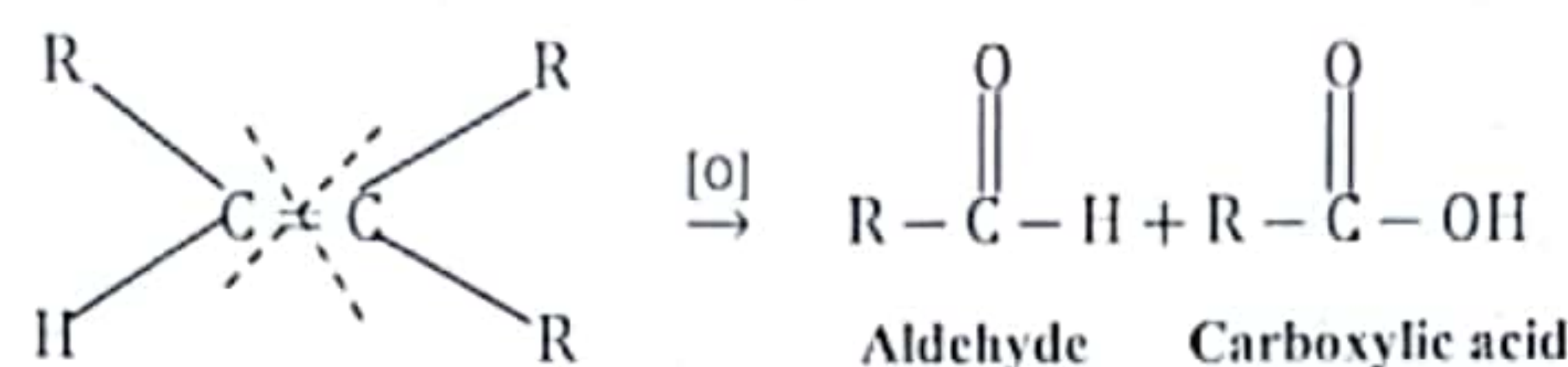
If each alkene carbon (carbon with $C = C$) is bonded to a hydrogen atom, a pair of either aldehyde or carboxylic acid is formed depending upon the reaction conditions.



Or



If one alkene carbon is bonded to a hydrogen atom and another alkene carbon is not bonded to any hydrogen atom, one molecule of aldehyde and one molecule of ketone is formed.



Important reactions to consider here are:

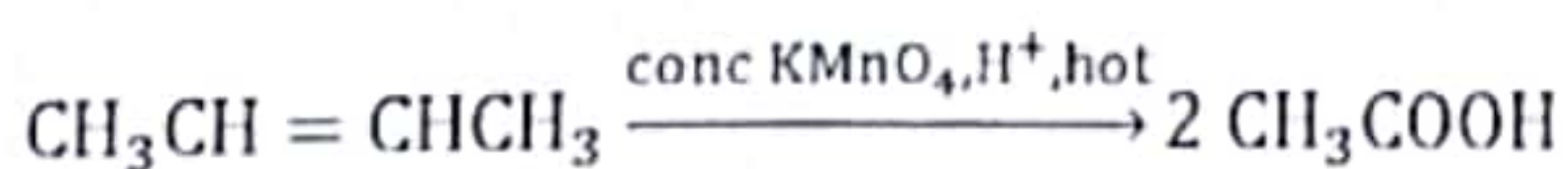
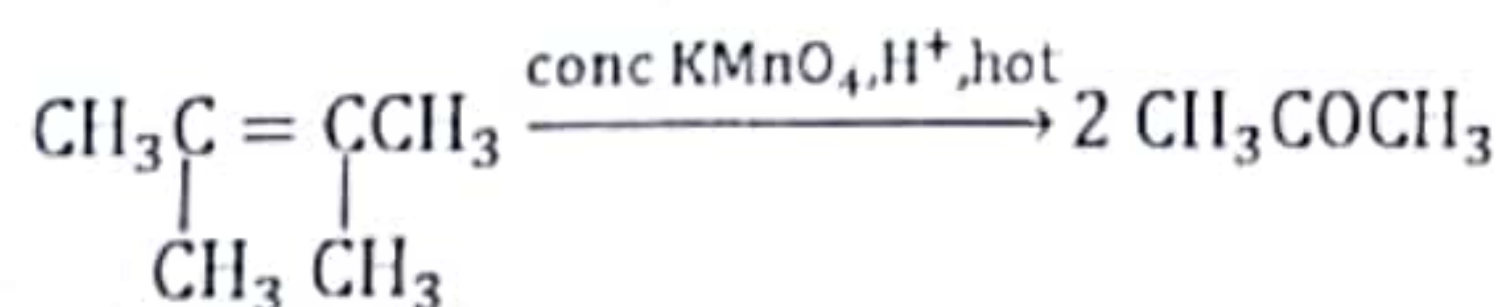
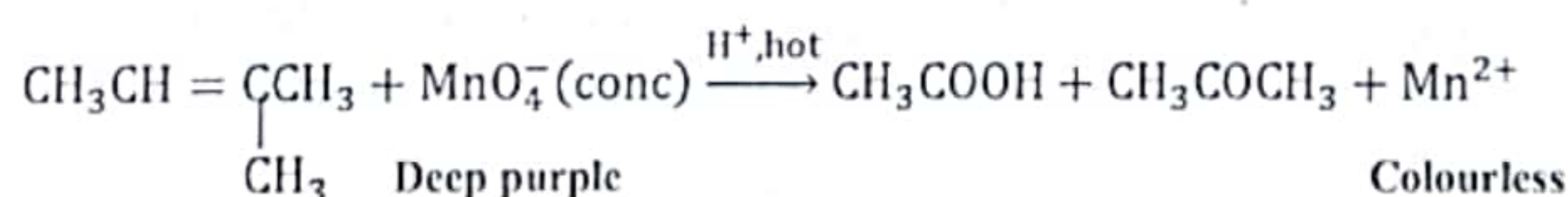
- Reaction of alkene with hot concentrated solution of acidified potassium permanganate
- Ozonolysis

Cleavage with hot concentrated solution of KMnO_4

A hot solution of acidified KMnO_4 is a vigorous oxidizing agent that leads to only ketones and carboxylic acids while KMnO_4 itself is reduced to colourless Mn^{2+} and its purple colouration disappear.

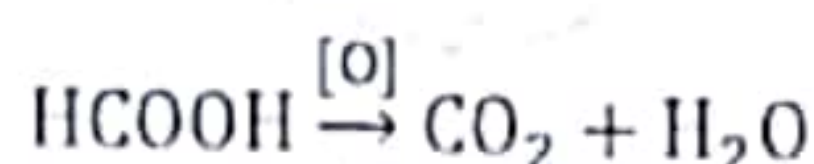
- Aldehydes cannot be isolated because are further oxidised to carboxylic acid.

Examples:

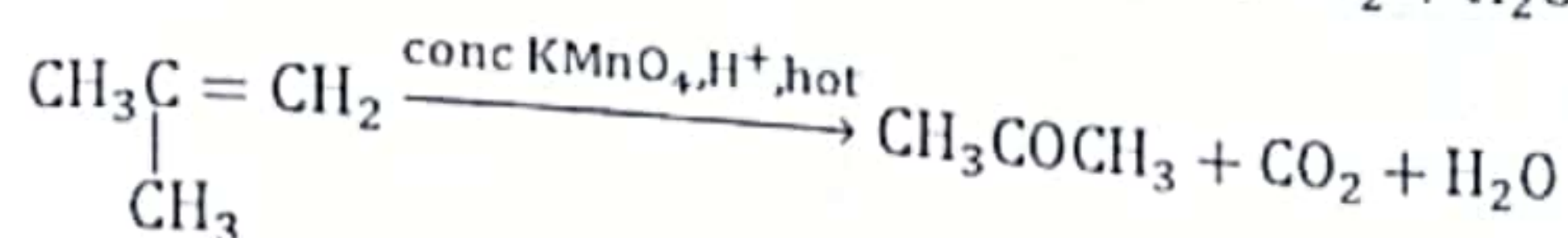
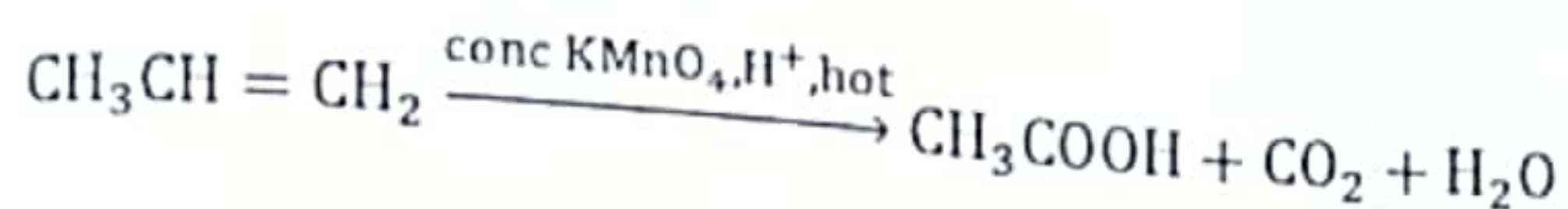


Under these vigorous oxidizing conditions, the carbon of a **terminal double bond** (double bond at the first carbon) is oxidised to CO_2 which appears as effervescence of colourless gas that turns lime water milky.

- CO_2 is formed because the methanoic acid (CH_3COOH) which would be formed is capable of undergoing further oxidation to CO_2 and H_2O .



Other mono-carboxylic acids do not undergo such reaction. They resist further oxidation.



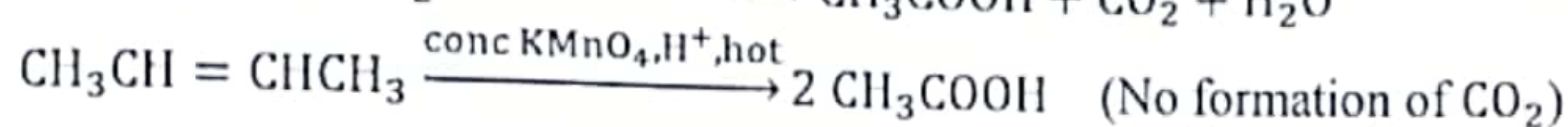
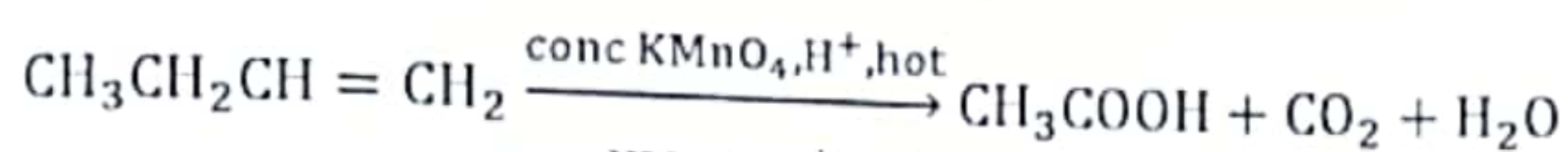
Therefore the reaction is very important in distinguishing alkene with terminal $\text{C}=\text{C}$ from alken without the terminal $\text{C}=\text{C}$.

Example 6

Give a chemical test to distinguish $\text{CH}_3\text{CH}=\text{CHCH}_3$ (but-2-ene) and $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ (but -1-ene).

Solution

With hot concentrated solution of acidified KMnO_4 , but-1-ene gives effervescence of colourless gas which turns lime water milky, i.e. CO_2 is formed while but-2-ene does not.



Question: Give 4 tests to distinguish between butane and but -2-ene.

Hints to a solution for the **Question**

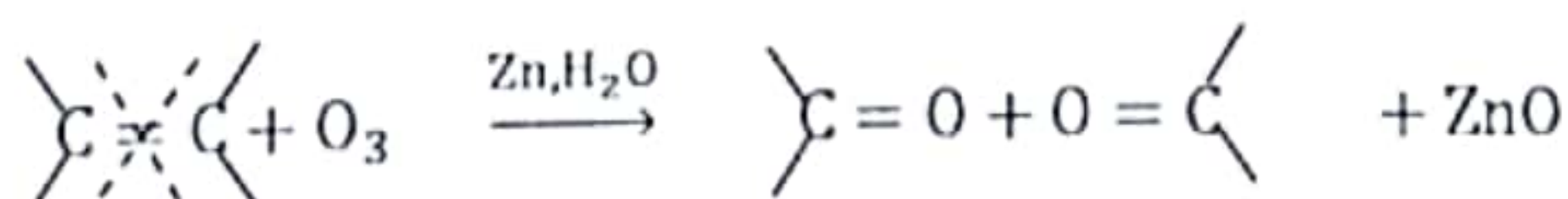
1. Reaction with bromine
2. Bromine water test
3. Baeyer test
4. Reaction with cold (at 0°C) concentrated sulphuric acid

Ozonolysis

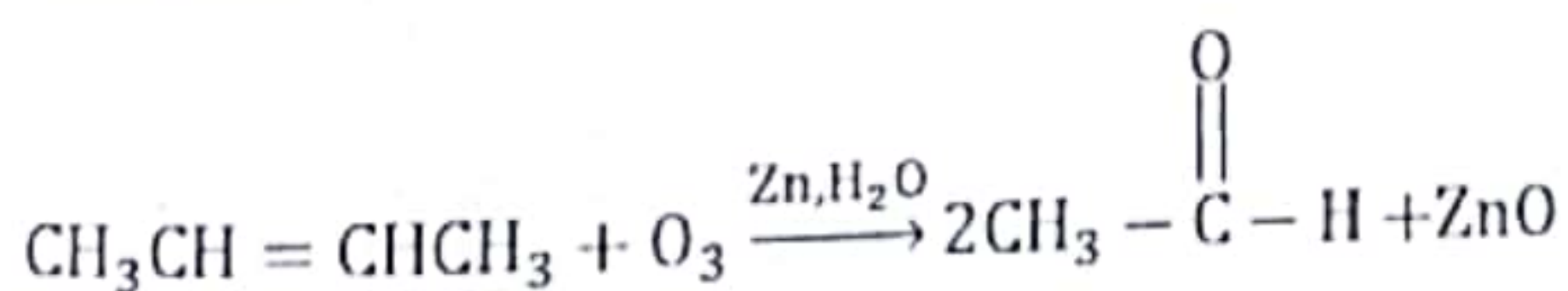
Alkene reacts with ozone under presence of water and zinc to form carbonyl compounds.

- The reaction consists of two separate reactions:
 1. Oxidation of the alkene by ozone to an **ozonide** and
 2. Hydrolysis of the ozonide under presence of zinc which is reducing agent and hence the term **reductive hydrolysis** for the second reaction.

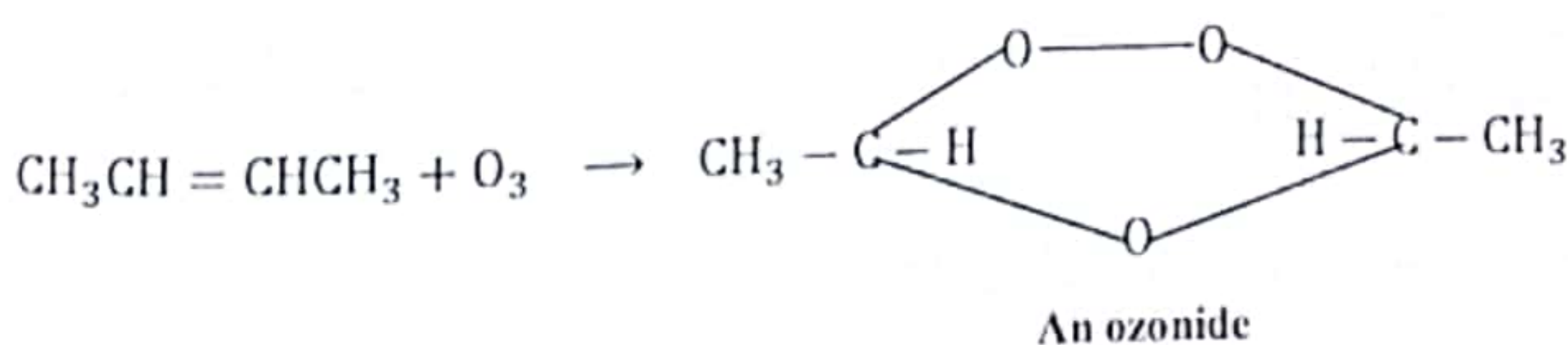
Generally;



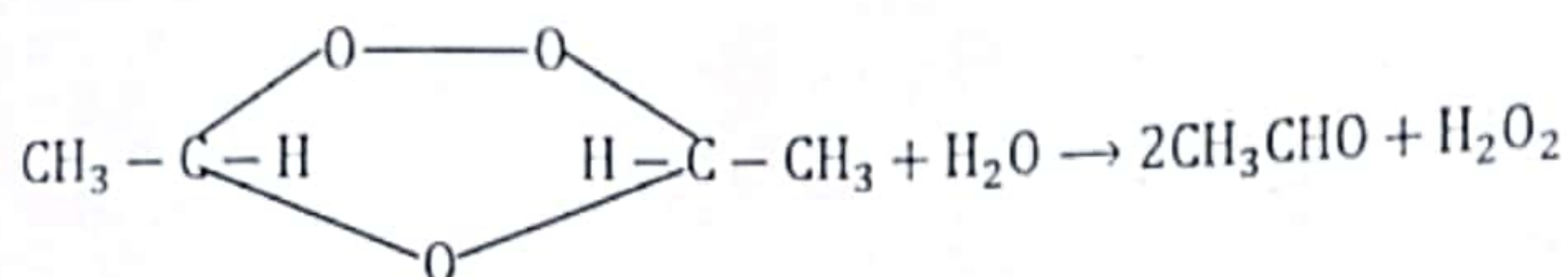
Example



But;



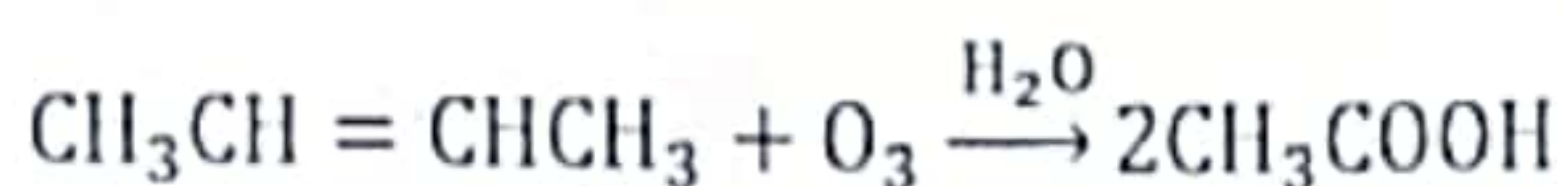
Then;



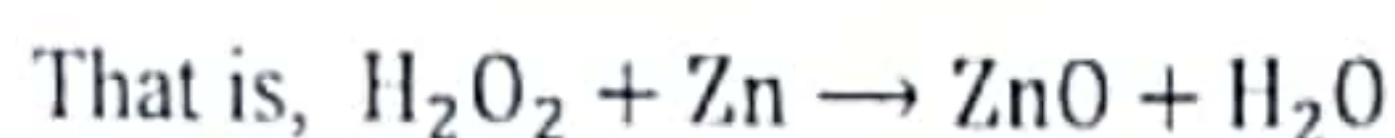
Under presence of aldehyde (CH_3CHO) which is reducing agent, hydrogen peroxide tends to oxidize the aldehyde to carboxylic acid and itself becomes reduced to water.



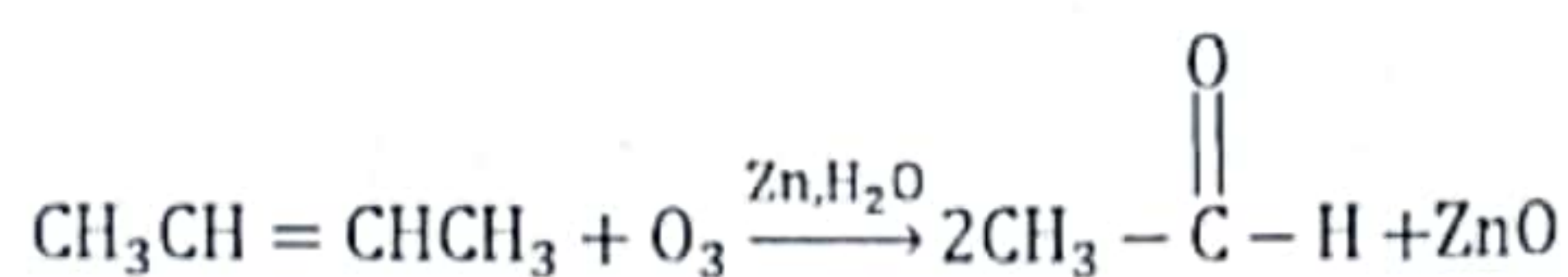
Thus the overall reaction equation between $\text{CH}_3\text{CH}=\text{CHCH}_3$ and O_3 followed by hydrolysis in absence of zinc can be written as follows:



But in presence of zinc which is stronger reducing agent than aldehyde, it tends to reduce the H_2O_2 to H_2O and itself being oxidised to ZnO thus preventing further oxidation of aldehyde to carboxylic acid.



And hence:



So the use of zinc in this reaction is to prevent further oxidation of aldehyde to carboxylic acid.

It should be noted that:

Ketones cannot undergo further oxidation even in absence of zinc because are not good reducing agents.

More examples of reactions between alkene and ozone in presence of water only (zinc is absent)

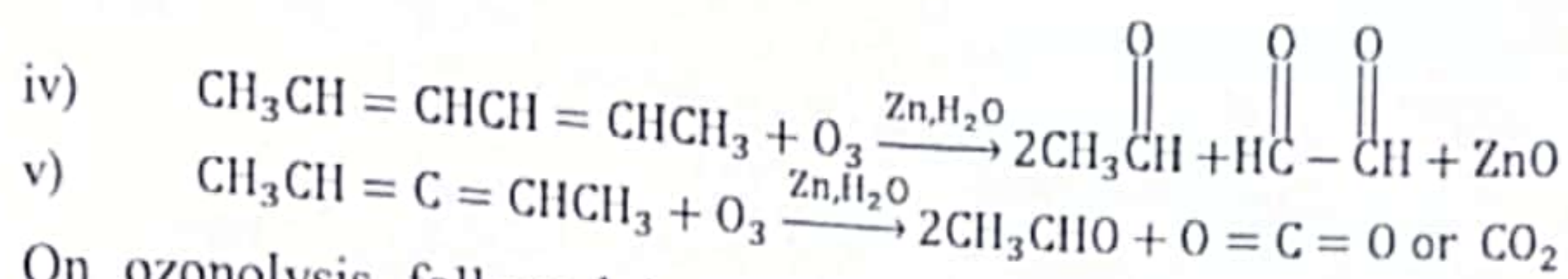
- i) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3 + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{COOH}$
- ii) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}=\text{CHCH}_3 + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{COOH}$
- iii) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}=\underset{\text{CH}_3}{\text{C}}\text{CH}_3 + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} 2\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}_2$
- iv) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} + \text{CO}_2$

The 4th example in (iv) above can be used as a test of presence of C – C terminal double bond in alkene. So it gives another test which distinguishes alkenes with terminal double bonds and those with no terminal double bonds. That is alkenes with terminal double bonds react with ozone under presence of water yielding effervescence of CO_2 gas which turns lime water milky while alkenes with no terminal double bond do not.

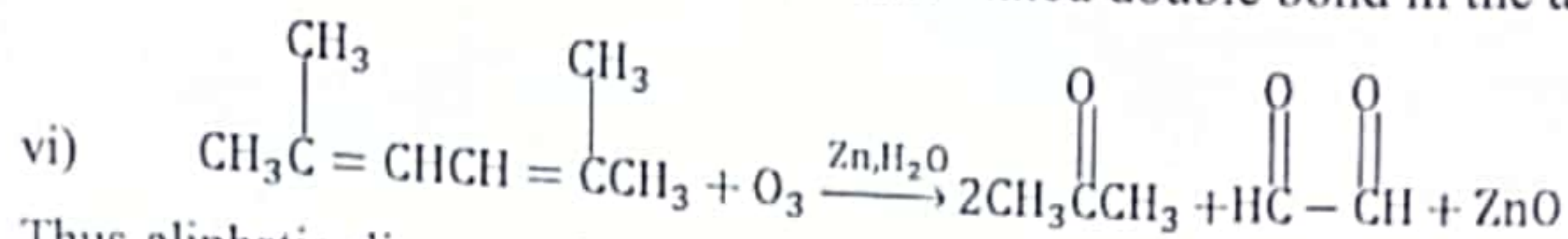
More examples of reactions between zinc and ozone followed by reductive hydrolysis

- i) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{O}_3 \xrightarrow{\text{Zn}, \text{H}_2\text{O}} \text{CH}_3\text{CHO} + \text{HCHO} + \text{ZnO}$
- ii) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}=\text{CHCH}_3 + \text{O}_3 \xrightarrow{\text{Zn}, \text{H}_2\text{O}} \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CHO} + \text{ZnO}$
- iii) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}=\underset{\text{CH}_3}{\text{C}}\text{CH}_3 + \text{O}_3 \xrightarrow{\text{Zn}, \text{H}_2\text{O}} 2\text{CH}_3\text{COCH}_3 + \text{ZnO}$

So ozonolysis of aliphatic alkenes with single carbon carbon double bond results to formation of two molecules of carbonyl compounds with single carbonyl group in each.



On ozonolysis followed by reductive hydrolysis, cumulated dienes liberate CO_2 which appears as the effervescence of colourless gas which turns lime water milky. So the reaction can be used as a test of presence of cumulated double bond in the alkene.



Thus aliphatic dienes undergo ozonolysis yielding three molecules of carbonyl compounds, i.e. two molecules with single carbonyl group in each and one carbonyl compound with two carbonyl groups.

The reader should understand that:

Products of obtained from ozonolysis of alkenes, enable to get correct structure of alkenes by giving position of double bond present in alkene originally reacted with ozone followed by reductive hydrolysis.

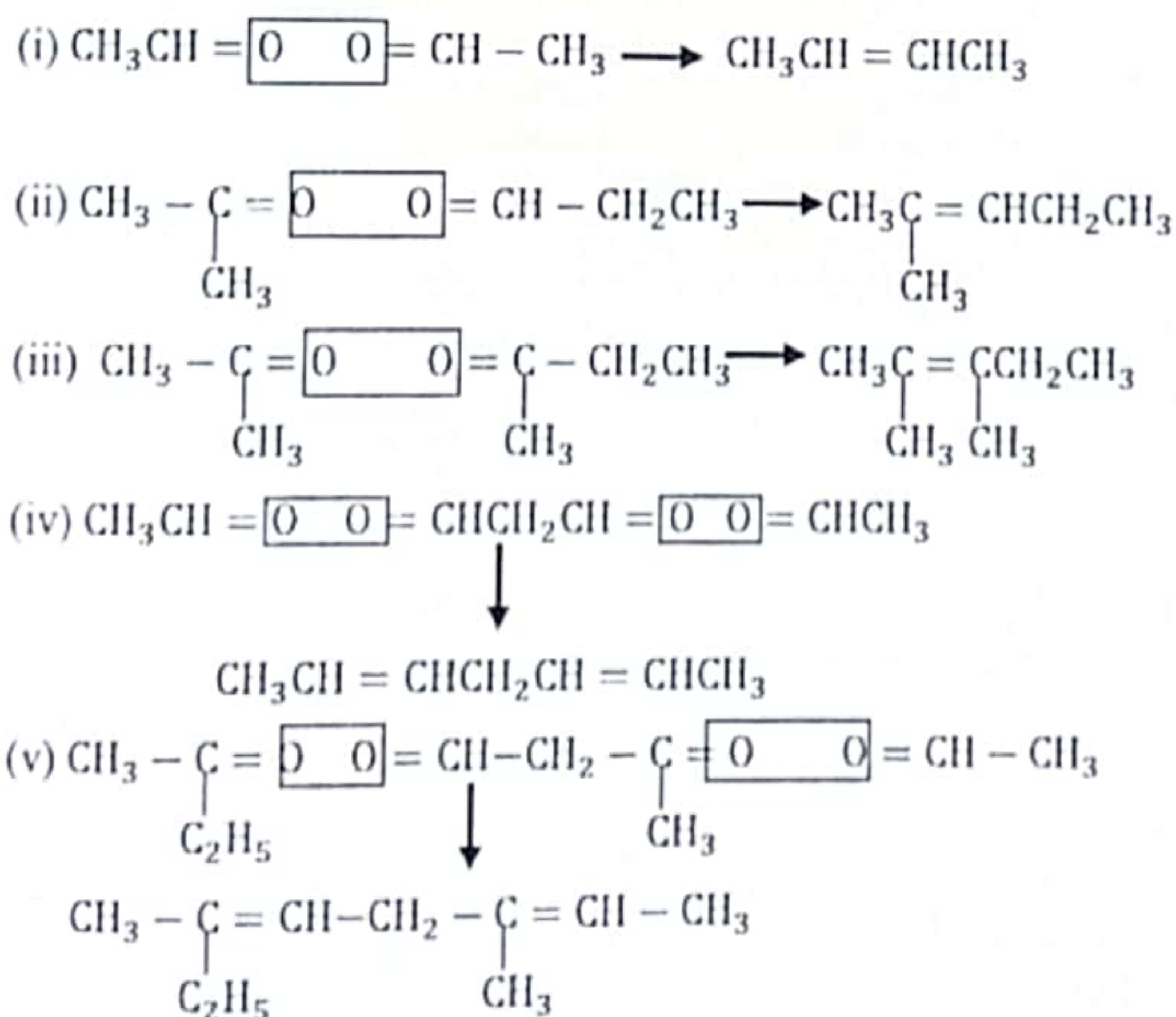
- This is simply done by removing oxygen from carbons of carbonyl groups and then the carbons are joined by double bond.

Example 7

Give structures of hydrocarbons which give the following products on ozonolysis.

- $2\text{CH}_3\text{CHO}$
- CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{CHO}$
- CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{COCH}_3$
- $2\text{CH}_3\text{CHO}$ and HOCH_2CHO
- $\text{CH}_3\text{COCH}_2\text{CH}_3$, $\text{HOCH}_2\text{COCH}_3$ and CH_3CHO

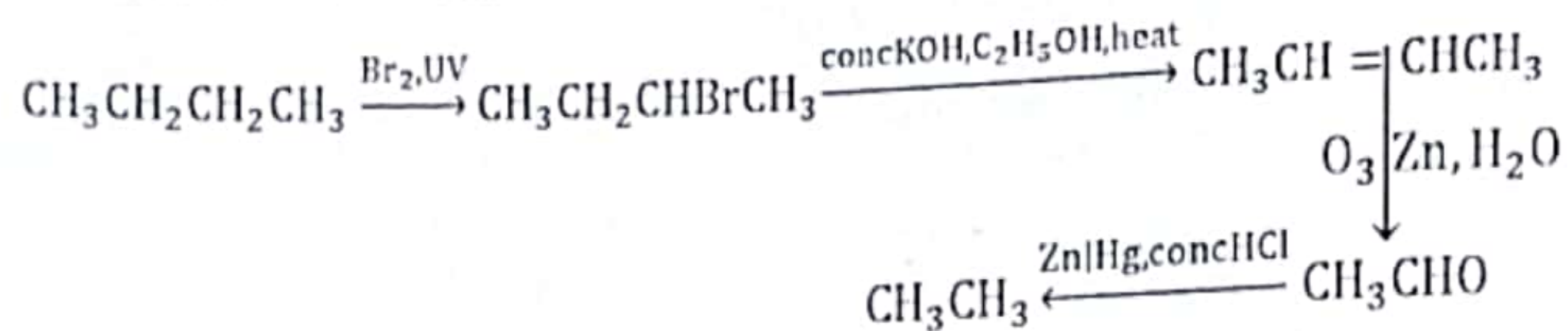
Solution



Last sentence to finish with ozonolysis!

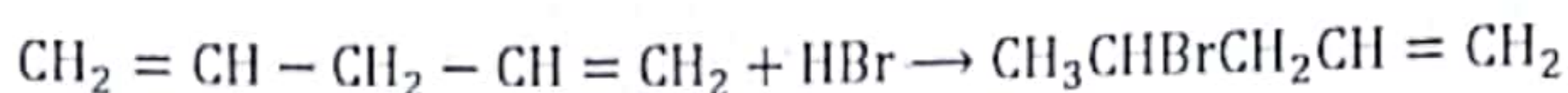
Ozonolysis is very important in dealing with conversion problems which decrease number of carbons especially when there is a possibility of having symmetrical alkene in order to avoid formation of mixture of organic products.

Example 8: Convert butane into ethane.



ELECTROPHILIC ADDITION REACTIONS OF DIENES

With limited amount of electrophilic reagent, cumulated dienes and isolated dienes react in the same way as alkenes with only one double bond, i.e. each double bond undergoes chemical reaction (addition reaction) separately. For example;

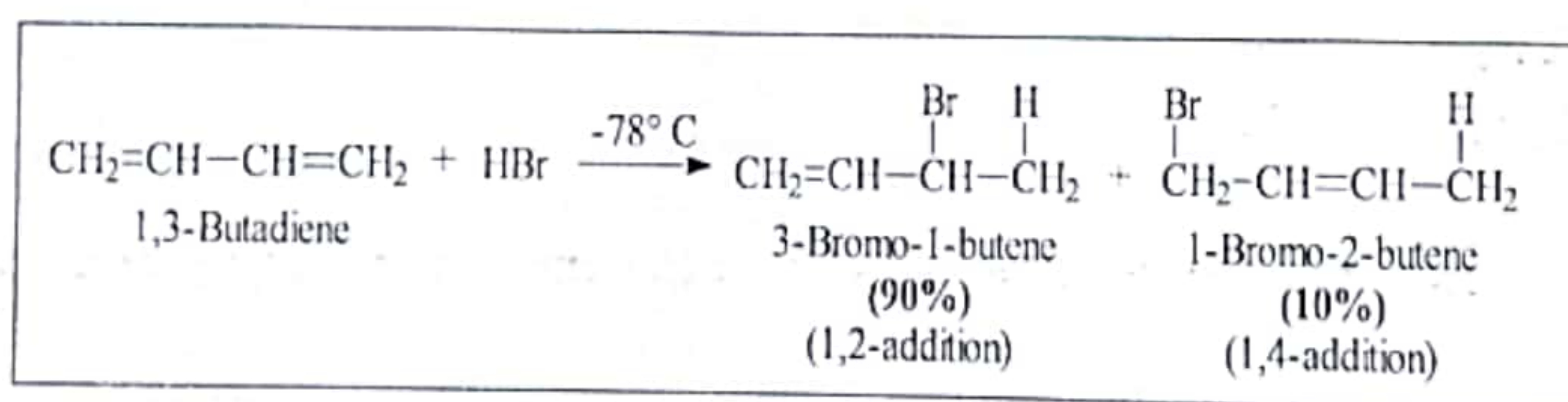


Conjugated double bond dienes show interesting property in addition reaction. They can undergo **1,2-addition reaction** (or **direct addition**) or **1,4-addition reaction** or **conjugate addition**.

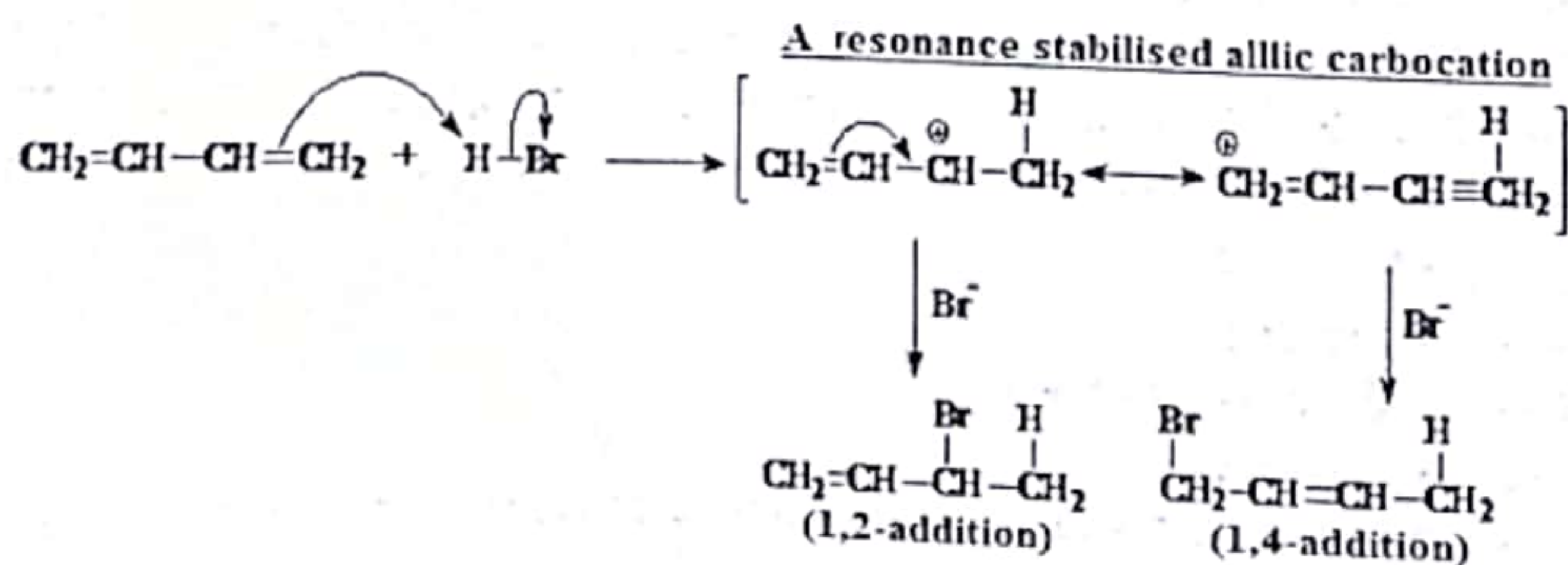
- In case of 1,4-addition reaction carbon-carbon double shift and atoms are added to first and 4th carbon while in 1,2-addition reaction position of double bond is conserved while atoms are added to first and second carbon).

Among the two products, **1,2-addition product** is formed at greater rate so it is a major product at low temperature. However at high temperature it is thermodynamically unstable and hence at high temperature **1, 4-addition product** which is more thermodynamically more stable becomes the major product.

- For example, when buta-1,3 diene is reacted with HBr at -78°C , both **1,2-addition product** (major product at this low temperature) and **1,4-addition product** are formed as per equation below:



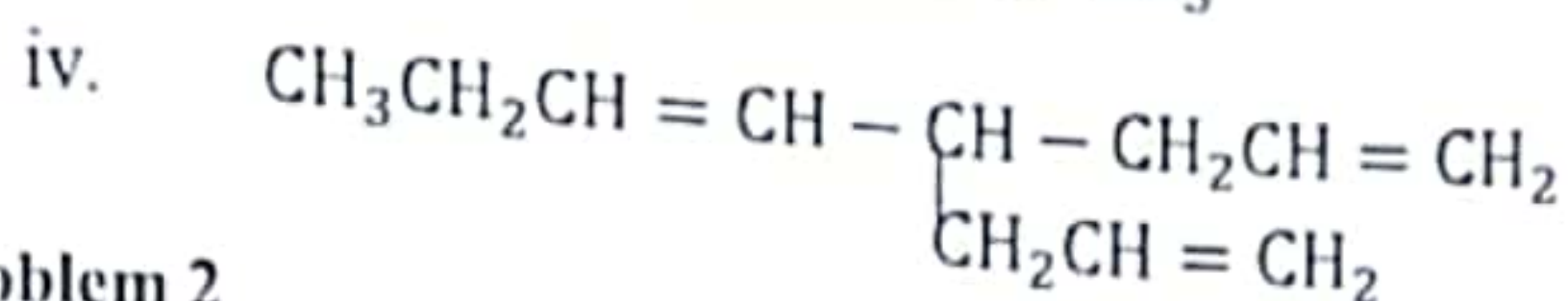
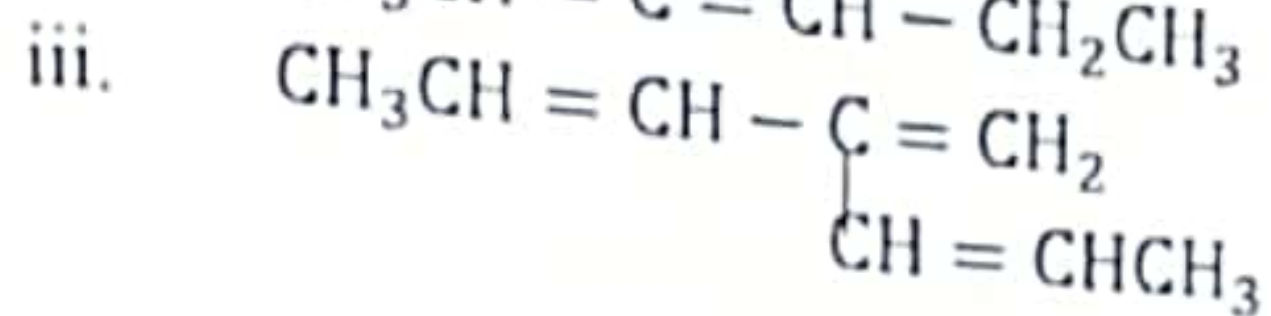
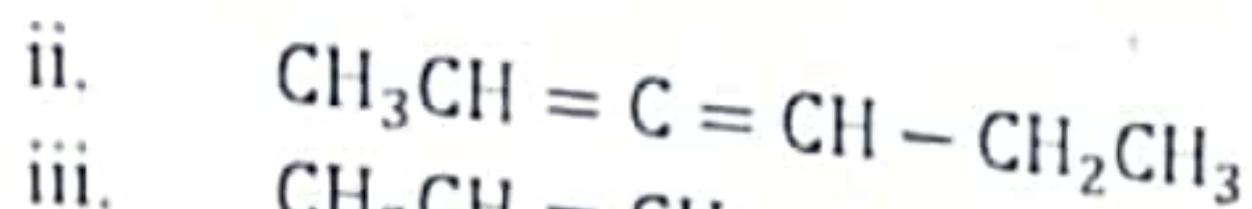
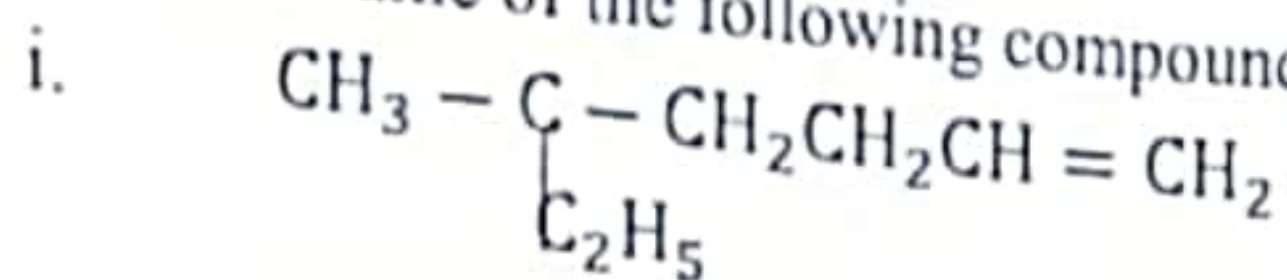
The formation of the two products is explained by mesomerism of the intermediate carbocation (carbenium ion) as the mechanism in the next page suggests:



PRACTICE EXERCISE 11

Problem 1

Give IUPAC name of the following compounds:



Problem 2

Give a structure and names of all possible geometric isomers of alkene with only four carbons.

Problem 3

By using bromohydrogenation of propene as an example, justify Markownikoff's rule.

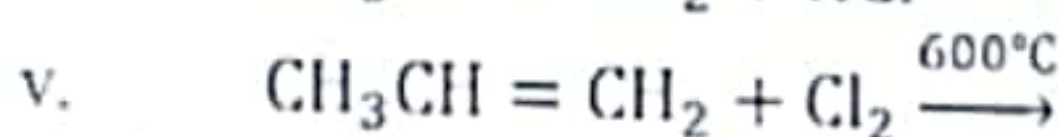
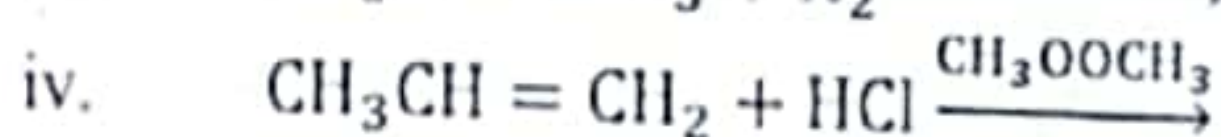
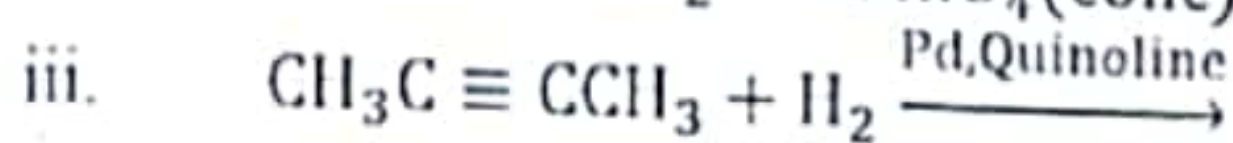
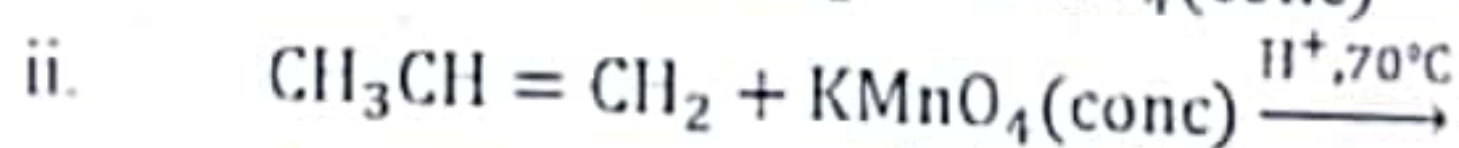
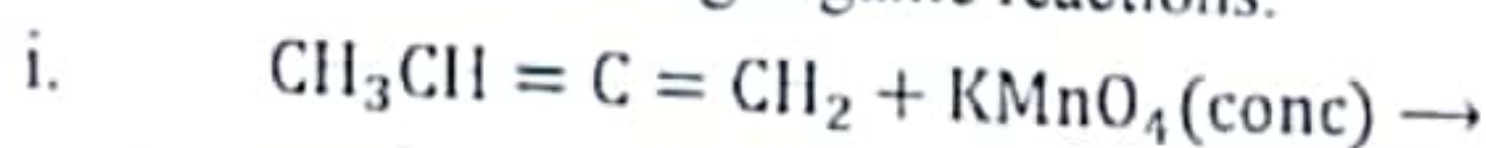
Problem 4

Write balanced chemical equation to show preparation of ethene from:

- 1,1-dibromoethane
- 1-bromoethane
- Ethanol
- Ethyne
- Sodium succinate

Problem 5

Complete the following organic reactions:



Problem 6

For the reaction between one molecule of hexa-2, 4-diene and one molecule of hydrogen chloride, write structure of:-

- 2,3-additional product
- 2,5-additional product

Show clearly how the two products are formed.

Problem 7

Rose is your friend who study advanced chemistry. She was given a home – work of IUPAC naming of organic compounds but was unable to give correct names for four structures. The bad news is that, she had lost a question paper and there is no way of getting it and her teacher need correction of the exercise while Rose has no idea of doing correction without having structures of organic compounds she failed to name. Below are incorrect names given by Rose in the home – work exercise:

- 2 – methypent-4-ene
- 4 – vinyheptane
- 6 – vinylhepta – 1,4-diene
- 3-ethylbut-1-ene

If Rose came to you and asks for your help in doing correction; what would be your help to her (includes drawings of missed structures).

Chapter 12 ALKYNES

Alkynes are unsaturated hydrocarbons with carbon-carbon triple bond ($C \equiv C$) as functional group.

- Aliphatic alkynes with only one carbon-carbon triple bond have general molecular formula of C_nH_{2n-2} .
- Thus aliphatic alkynes with only one carbon-carbon triple bond are functional isomers to aliphatic dienes.

SYSTEMATIC Nomenclature of Alkynes

Rules of naming alkynes are the same as those of naming alkanes with the following modifications:

- The parent chain must contain carbon-carbon triple bond, i.e. the parent chain is the longest continuous carbon chain with $C \equiv C$.
- Numbering of carbons in the parent chain starts at the end closer to $C \equiv C$.
- Position of $C \equiv C$ should be indicated by using Arabic numerals and the position shown should be that of first carbon with carbon-carbon triple bond ($C \equiv C$).
- The parent name should end with suffix -yne.

Alkynes as substituents

As substituents, alkynes are named as **alkynyl**.

- If the alkynyl group has 2 carbons there is no need of showing position of $C \equiv C$ because with 2 carbons there is only possibility of inserting the triple bond. But if the alkynyl group has more than 2 carbons, the position of $C \equiv C$ must be indicated; and the attaching carbon must be given first position. For example:

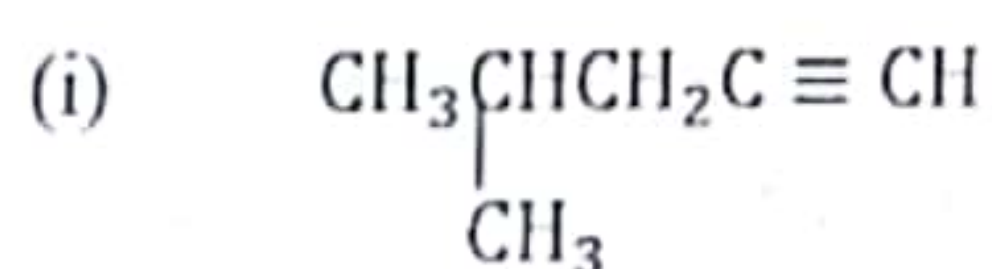
$CH \equiv C -$ is named as **ethynyl**

$CH_3C \equiv C -$ is named as **1-propynyl** (to differentiate it from $CH \equiv CCH_2 -$ which is **2-propynyl**)

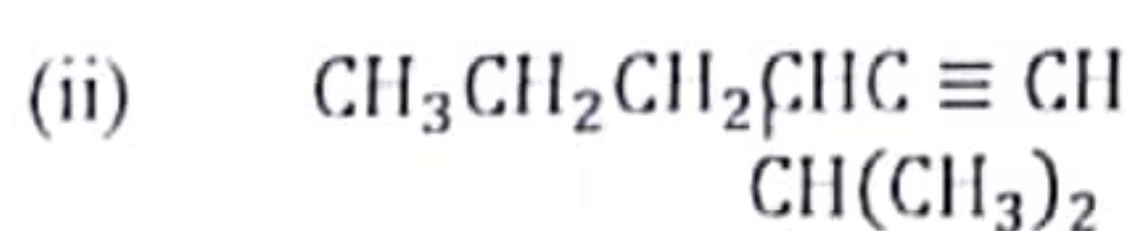
$CH_3C \equiv CCH_2 -$ is named as **2-butynyl** (to differentiate it from $CH_3CH_2C \equiv C -$ which is **1-butynyl** or $CH \equiv CCH_2CH_2 -$ which is named as **3-butynyl**)

Example 1

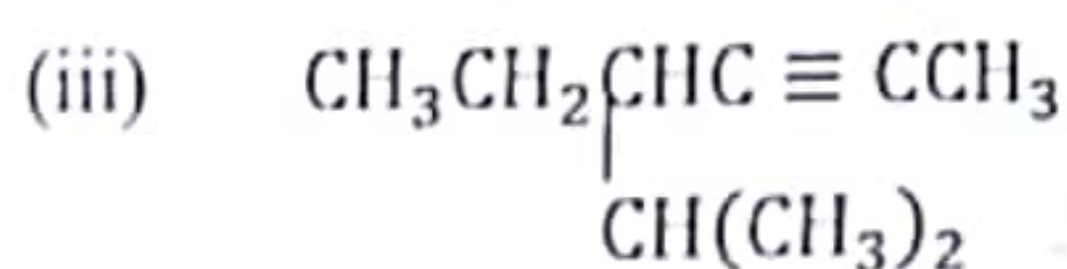
Name the following organic compounds:



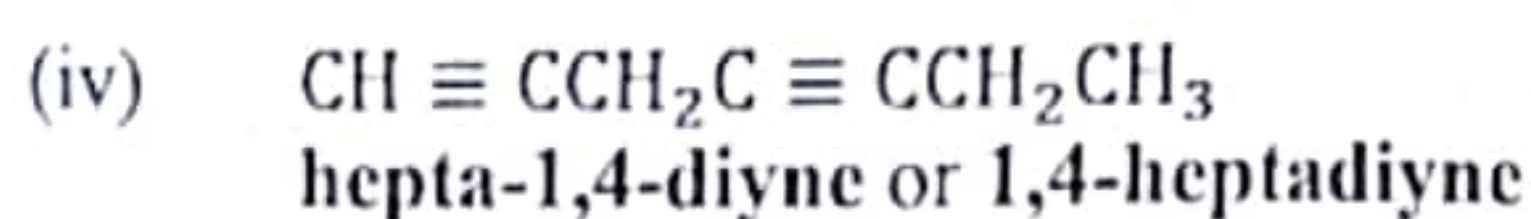
4-methylpent-1-yne or **4-methyl-1-pentyne**



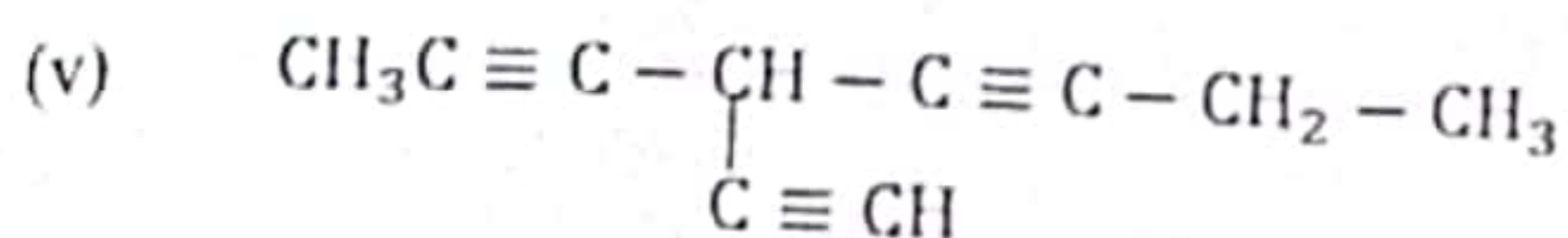
3-isopropylhex-1-yne or **3-isopropyl-1-hexyne**



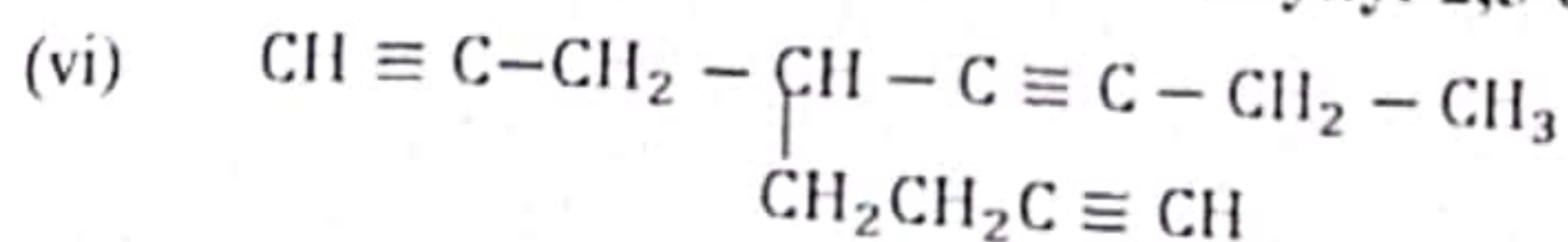
4-ethyl-5-methylhex-2-yne or **4-ethyl-5-methyl-2-hexyne**



(Notice the insertion of 'a' before 'di' of diyne. The vowel 'a' is retained in the stem like in the case of diene)



4-ethynylocta-2,5-diyne or 4-ethynyl-2,5-octadiyne



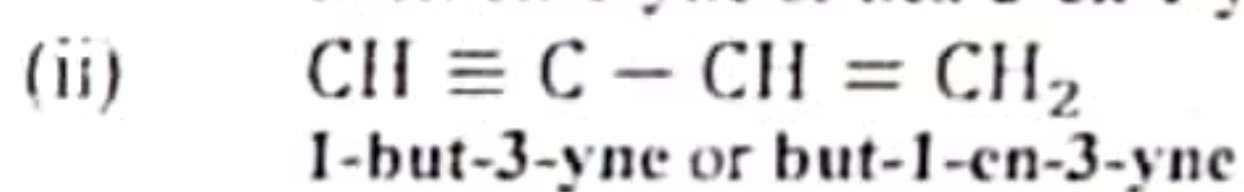
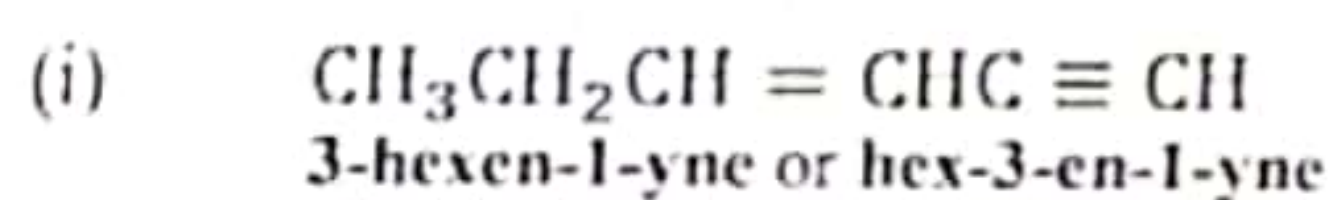
5-(2-propynyl)nona-1,6-diyne or 5-(2-propynyl)-1,6-nonadiyne

Naming a molecule containing both triple bond and double bond

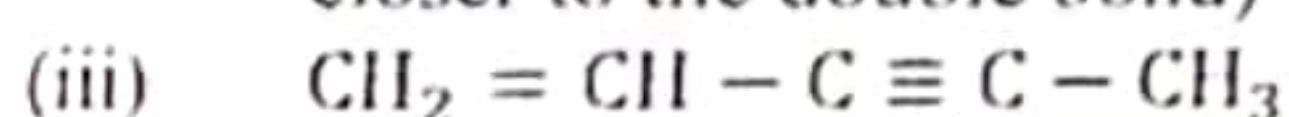
- If a molecule contains both a double and a triple bond, the carbon chain is numbered so that the **first multiple bond gets a lower number**.
- If both bonds can be assigned the same number, the double bond takes precedence (numbering starts at the end closer to the double bond).
- The molecule is then named in such a way that the double bond root name is written before the triple bond root name (e.g. 2-hepten-4-yne or hept-2-en-4-yne).

Example 2

Name the following organic compounds:



(Here from either end, multiple bond is at the first carbon so numbering must start at the end closer to the double bond)



1-penten-3-yne or pent-1-en-3-yne

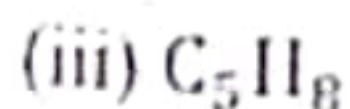
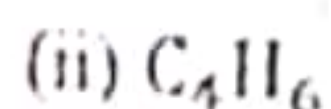
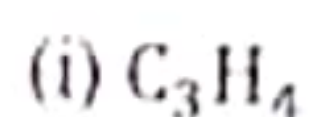
ISOMERISM IN ALKYNE

Alkyne exhibits the following types of isomerism;

- Skeletal/chain isomerism
- Position isomerism
- Functional isomerism

Question

Name all possible isomers of compounds with the following molecular formulae:



PREPARATIONS OF ALKYNES

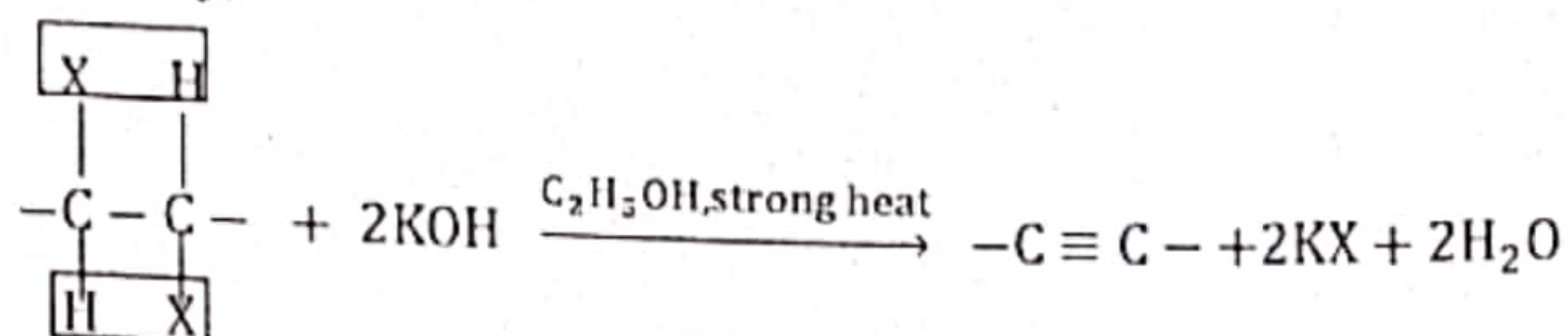
The preparations of alkynes are very similar to those of the alkenes. The main preparative reactions involve the elimination of groups from molecules, resulting in the formation of $\text{C} \equiv \text{C}$.

Dehalohydrogenation of dihaloalkanes

Dihaloalkane reacts with concentrated solution of KOH under presence of alcoholic medium and heat to give alkyne.

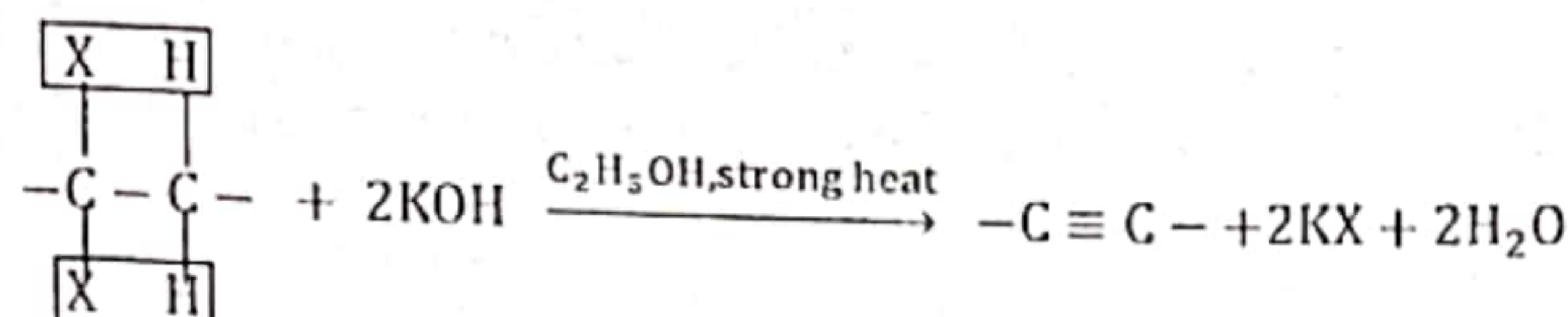
- The dihaloalkane may be **geminal** (halogens at the same carbon) or **vicinal** halide (halogens at adjacent carbon atoms).

Generally;

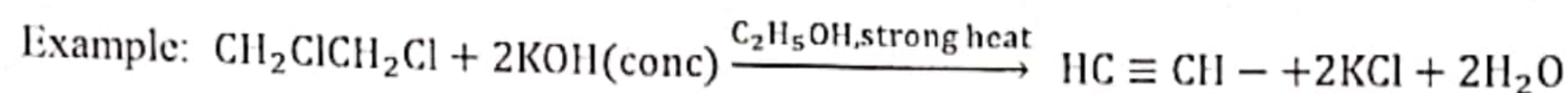


Vicinal halide

Or

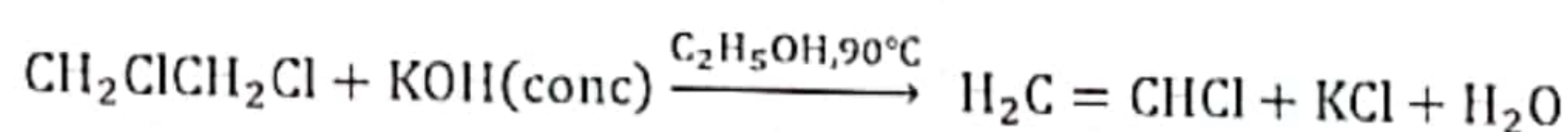


Geminal halide



In the above reaction, when the temperature is 200°C , the formation of the alkyne is assured.

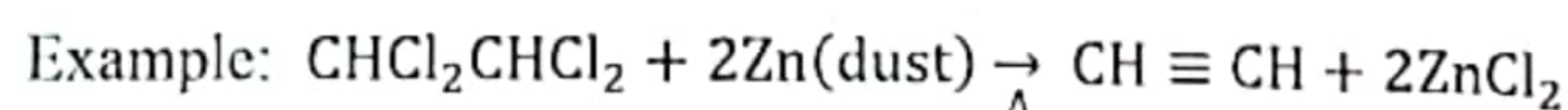
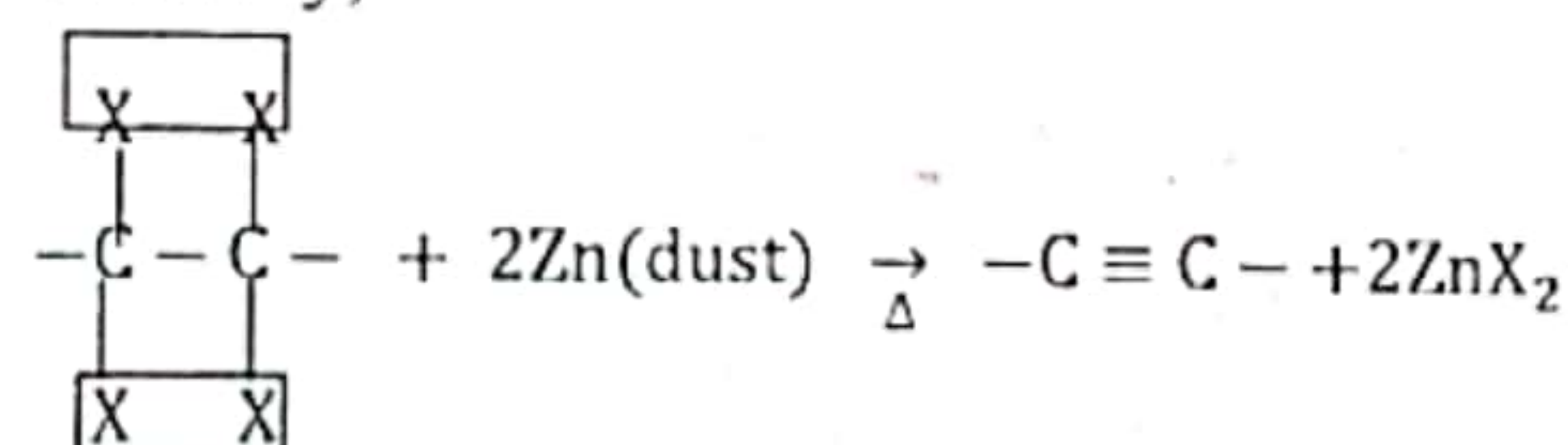
- When the temperature is 90°C , the elimination is incomplete and vinyl chloride (chloroethene) is formed.



Dehalogenation of tetrahaloalkanes

Four halogens from adjacent carbon atoms of haloalkane are eliminated resulting to formation of $\text{C} \equiv \text{C}$ between the two carbons when the compound is heated with zinc dust.

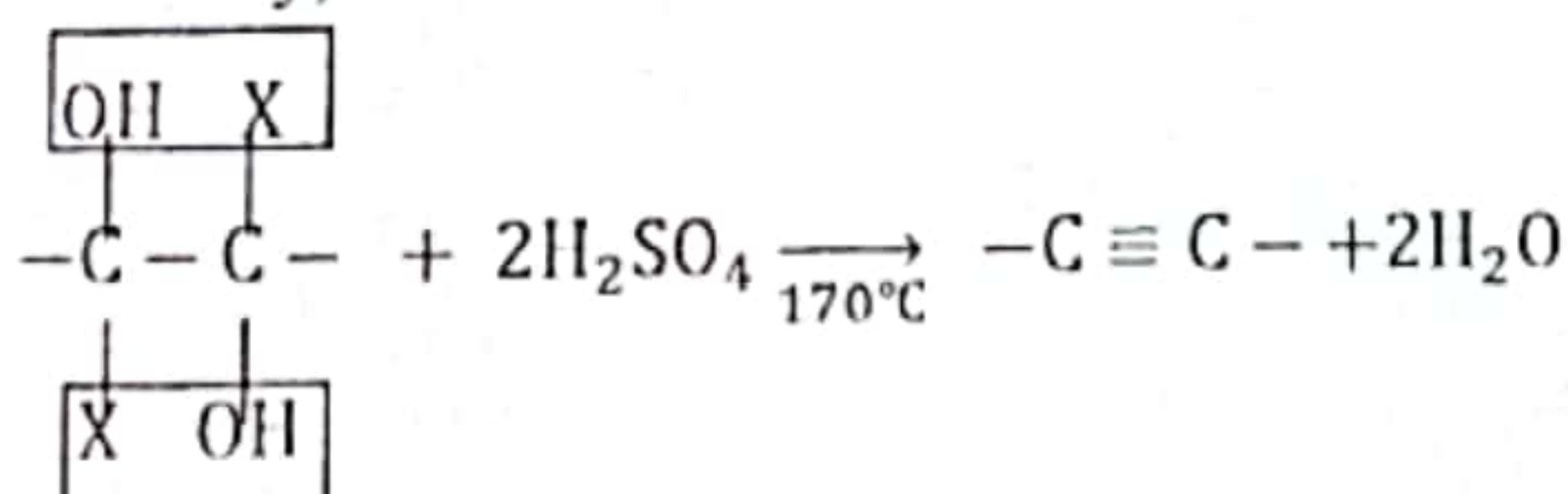
Generally;



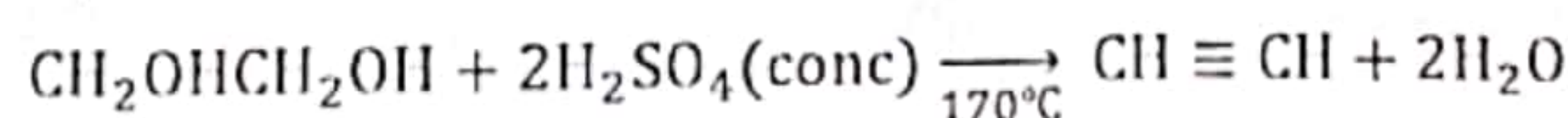
Dehydration of diols

With concentrated sulphuric acid under presence of heat, diol undergoes β elimination reaction to give alkyne.

Generally;



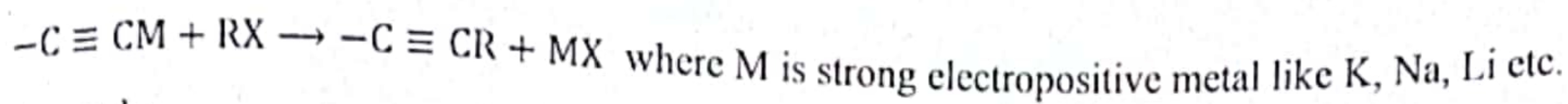
Example;



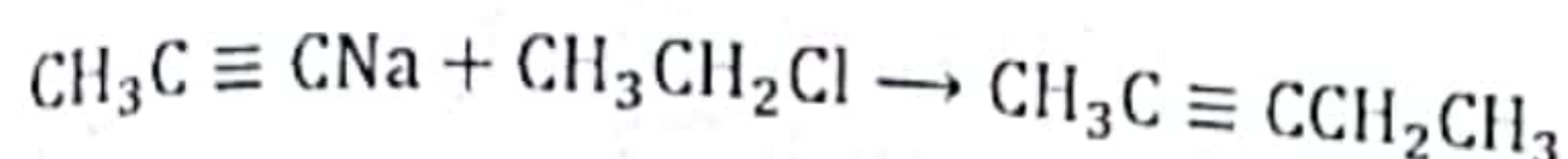
Alkylation of acetylide ion

Negatively charged acetylide ion ($-\text{C} \equiv \text{C}^\ominus$) reacts with haloalkane to form alkyne.

Generally;



Example

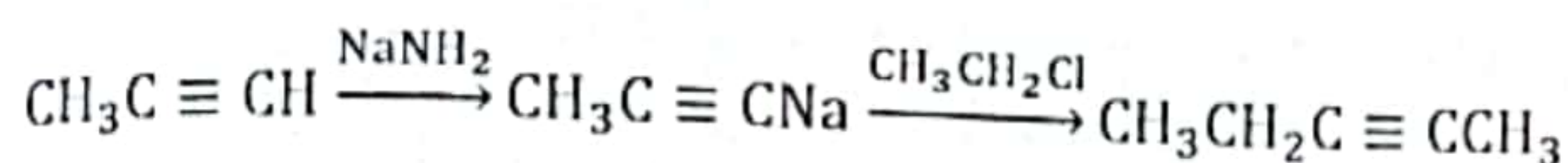


In the above reaction there is an increase in number of carbons; so the reaction is very important in dealing with conversion problems which show that there is an increase in number of carbons (number of carbon atoms can be increased at any extent depending on the number of carbons present in alkyl group).

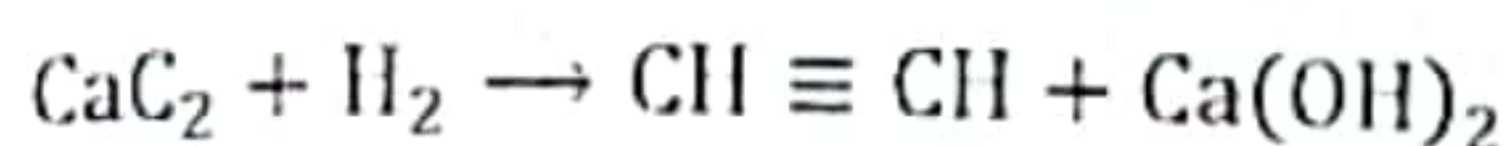
Example 3

Show how you can convert $\text{CH}_3\text{C} \equiv \text{CH}$ into $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CCH}_3$

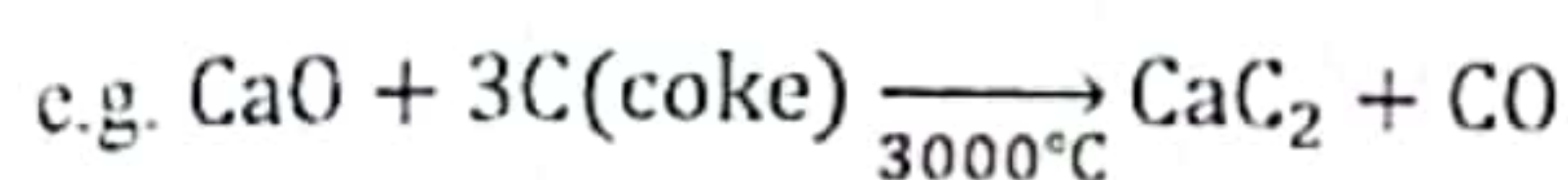
Solution

**Hydrolysis of calcium carbide**

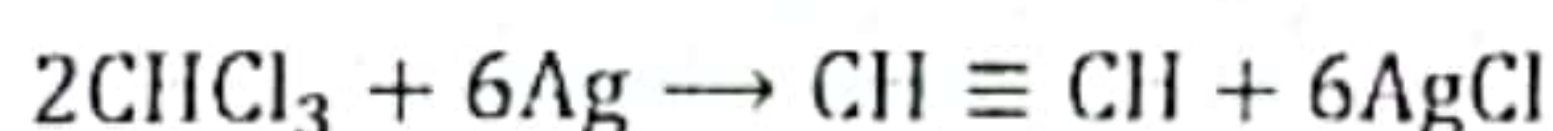
When calcium carbide is heated with water, ethyne is formed.



The CaC_2 is produced by heating the mixture of CaO and coke (carbon) at temperature which is not less than 2500°C .

**Reaction between chloroform (trichloromethane) and silver**

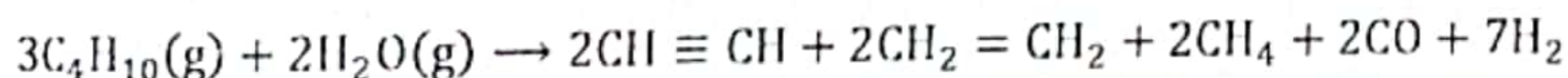
When chloroform is heated with silver powder, ethyne is formed.

**Production of ethyne by thermal cracking**

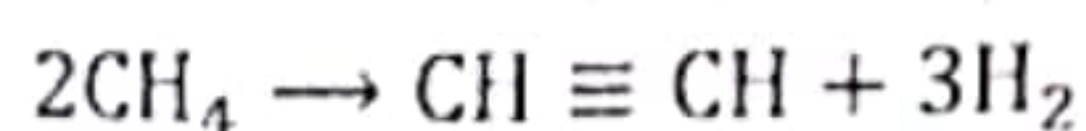
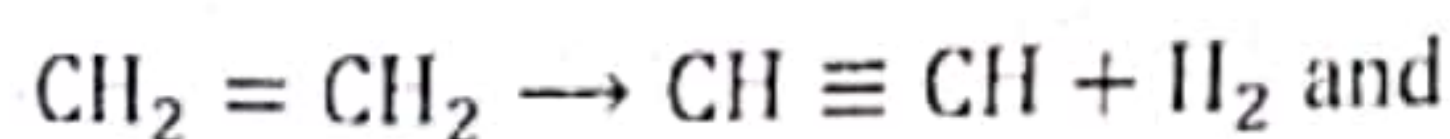
Ethyne is made industrially from hydrocarbons obtained by cracking petroleum.

- This is done by the thermal cracking of butane with steam as a diluent. The production of ethyne by this method is done in series of chemical reactions as shown below.

Firstly;



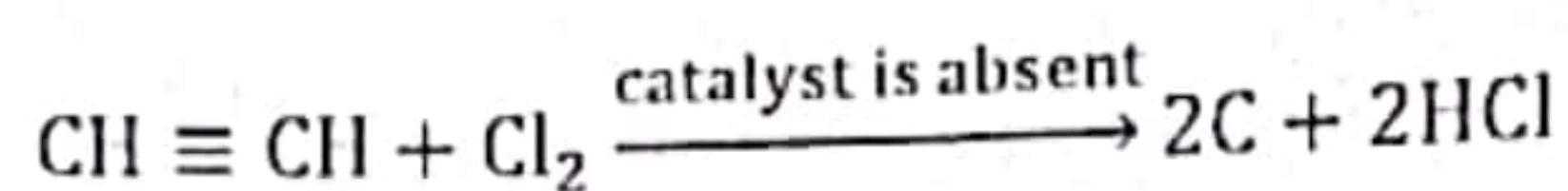
Subsequent reactions in this gas stream are:

**CHEMICAL REACTIONS OF ALKYNES**

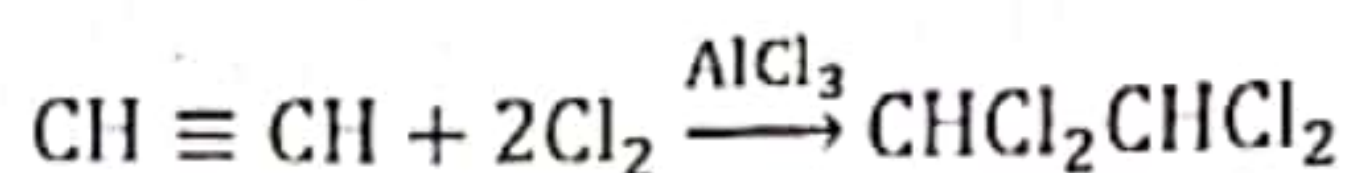
Most of reactions of alkynes are the same as those of alkanes but may differ in their reacting conditions.

Halogenation

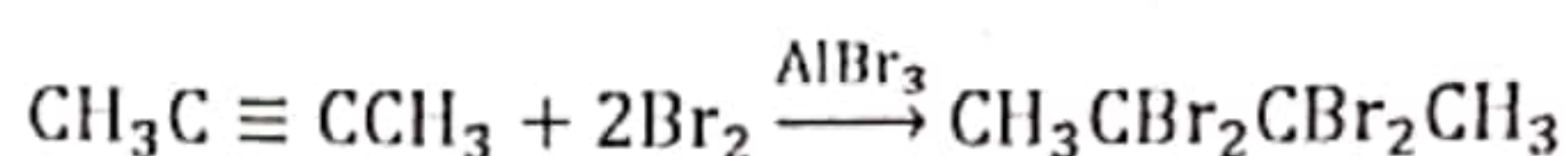
In absence of catalyst (Lewis acid) ethyne gives black soot and red flame with halogens particularly chlorine (of course, and fluorine whose reaction with the alkyne is explosive) which is very reactive.



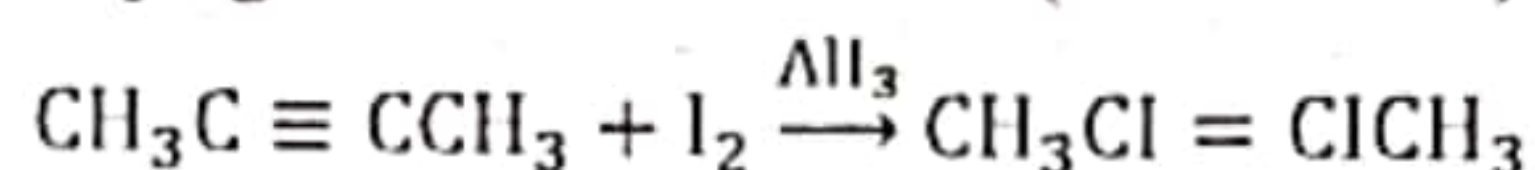
But in presence of Lewis acid (e.g. AlCl_3 and FeCl_3), it reacts to form more useful additional product according to the equation;



Similarly;



Iodine being least reactive of all halogens it leads to cleavage of one π only under normal conditions and therefore iodine commonly gives diiodoalkene (unsaturated) with alkyne. For example;



Cl_2 and Br_2 commonly leads to cleavage of all two π bonds thus forming tetraalkane (saturated) unless their amount is very small compared to the amount of alkyne.

It should be understood that:

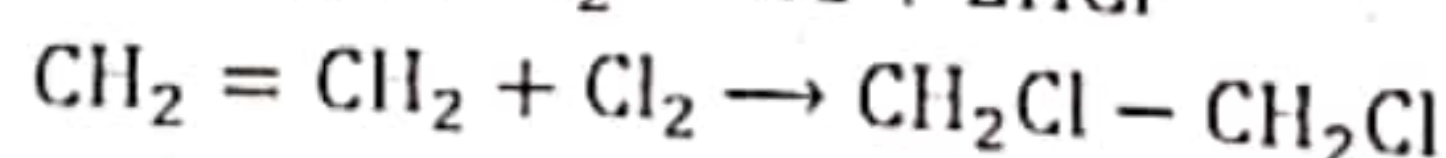
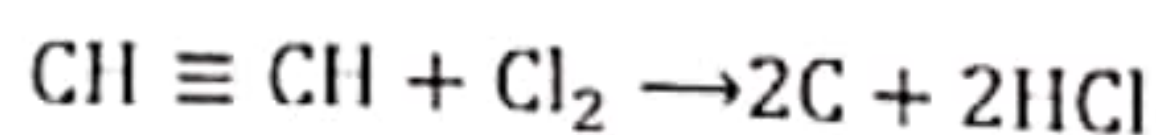
Formation of black soot and red flame when ethyne and chlorine are mixed gives a test which distinguishes ethyne from alkenes.

Example 4

How would you distinguish between ethene and ethyne.

Solution

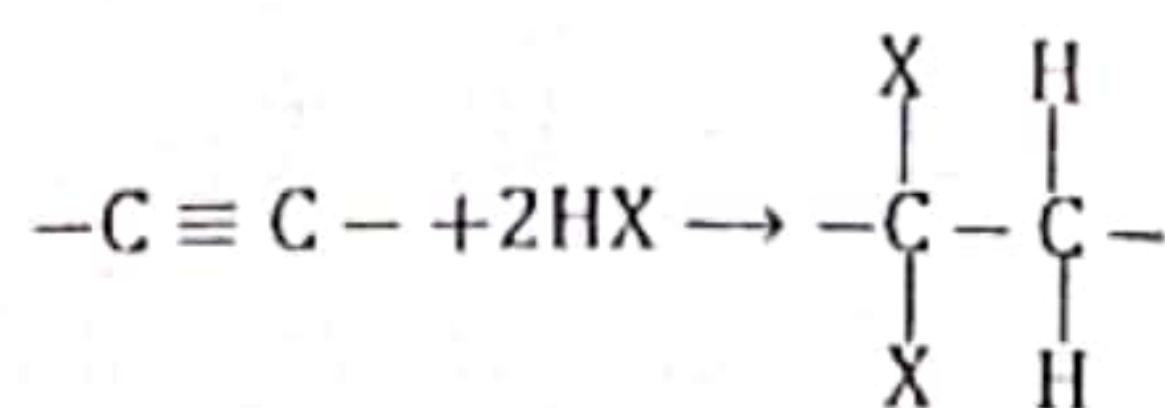
With chlorine, ethyne gives black soot of carbon and red flame while ethene does not.



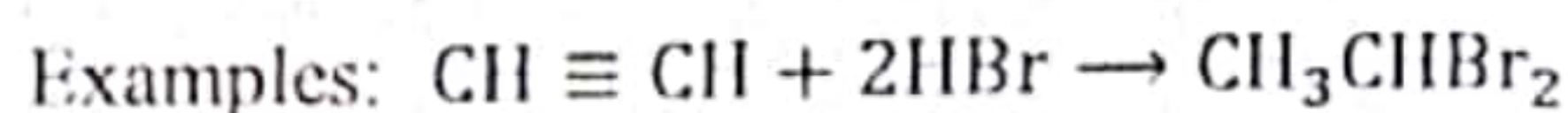
Halohydrogenation

Alkynes react with hydrogen halide yielding dihaloalkane.

Generally;



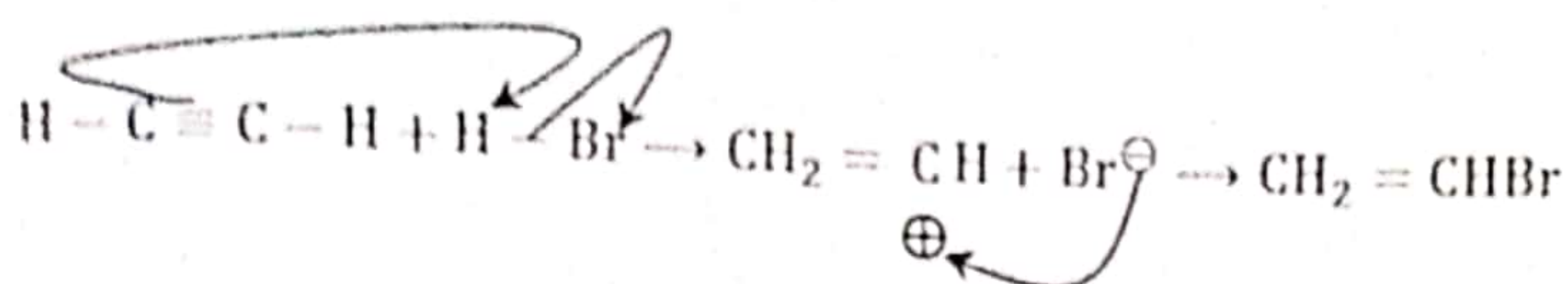
The reaction is electrophilic addition reaction so it follows Markownikoff's addition.



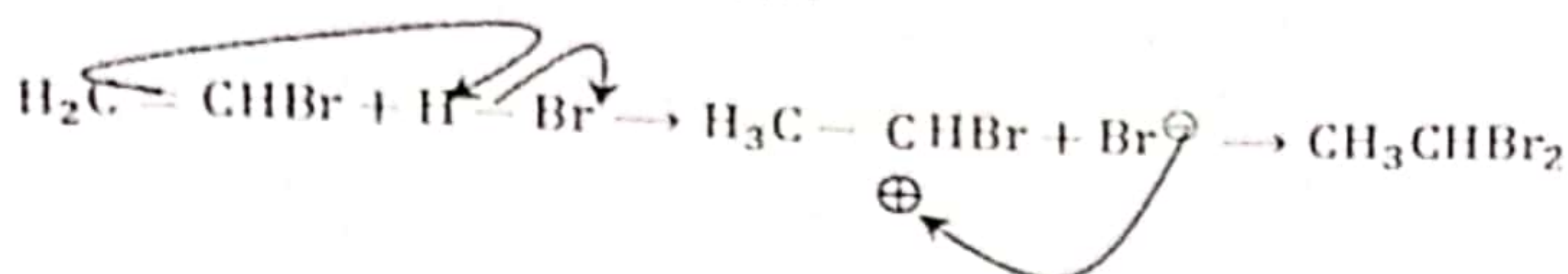
To get more stable intermediate carbenium ion on the addition of second molecule of, all two hydrogen atoms must be added to one carbon atom and all two bromine atoms are added to another carbon. (See mechanism below).

Mechanism

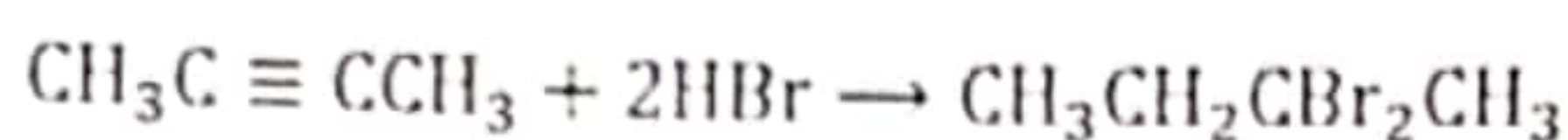
Addition of first molecule of HBr



Addition of second molecule of HBr

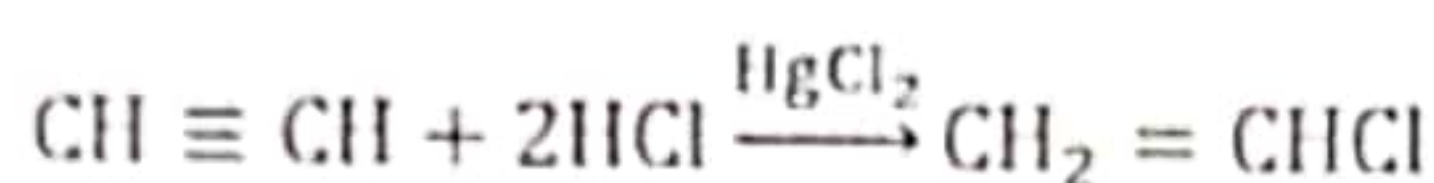


Other examples are:



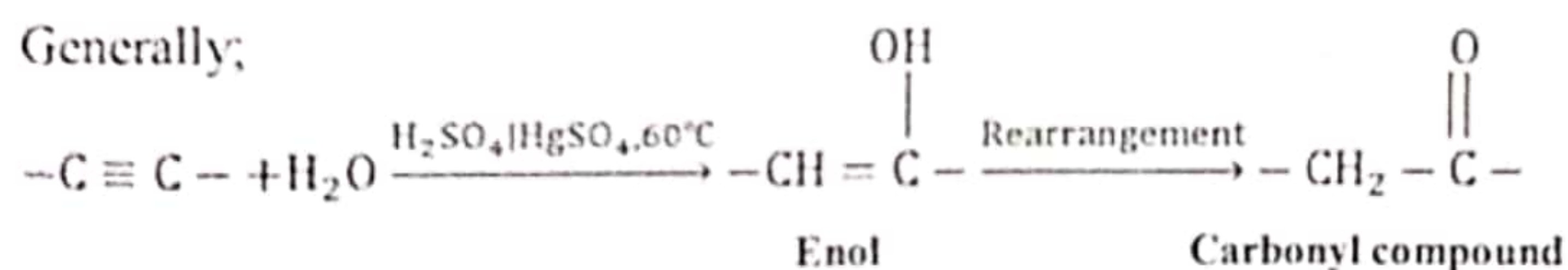
It should be noted that:

When hydrogen chloride is added to ethyne (its common name is **acetylene**) in presence of mercuric chloride, vinyl chloride (chloroethene) is formed.

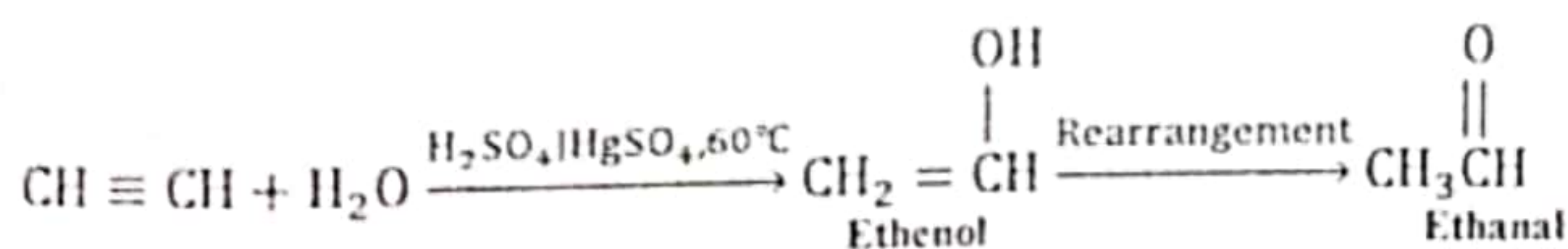


Hydration

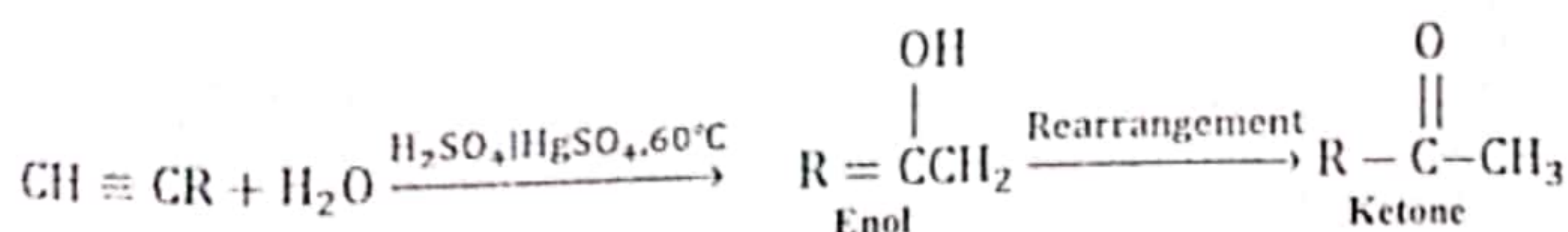
Alkyne reacts with water under presence of sulphuric acid and mercury sulphate as catalyst to give enol (unstable) which on rearrangement gives carbonyl compound (more stable).



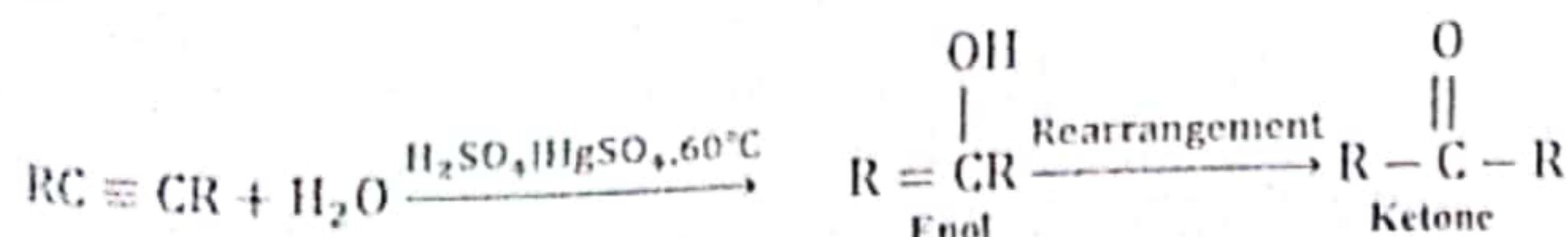
Ethyne gives ethanal (aldehyde).



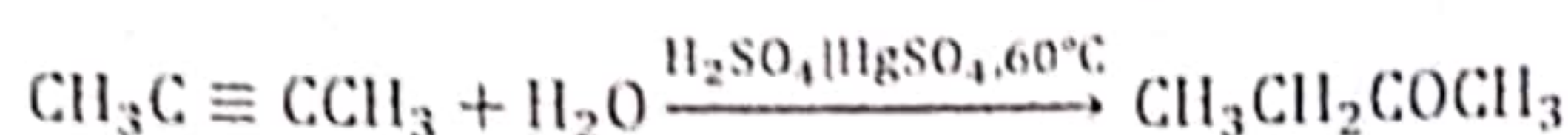
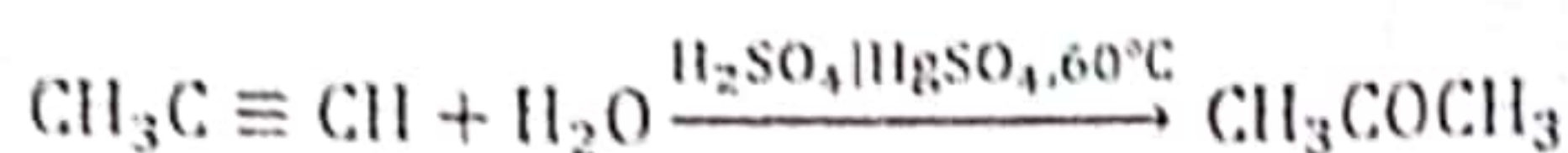
Higher members of alkyne give ketones.



Or



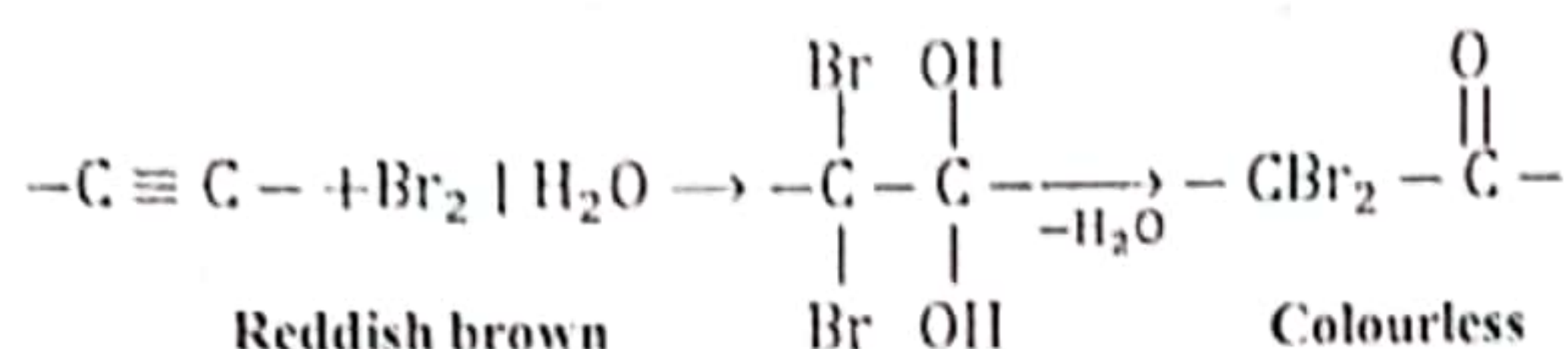
Examples:



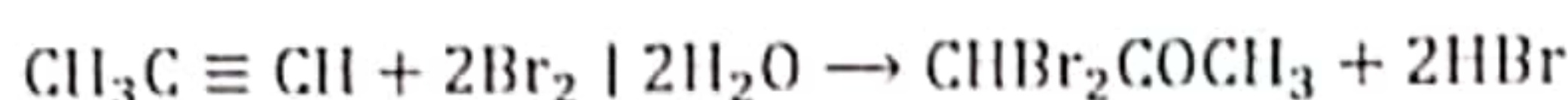
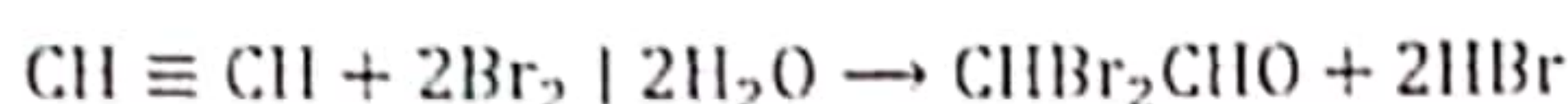
Reaction with bromine water

Like alkenes, alkynes decolourise bromine water, i.e. alkynes give positive bromine water test which is the test of unsaturation.

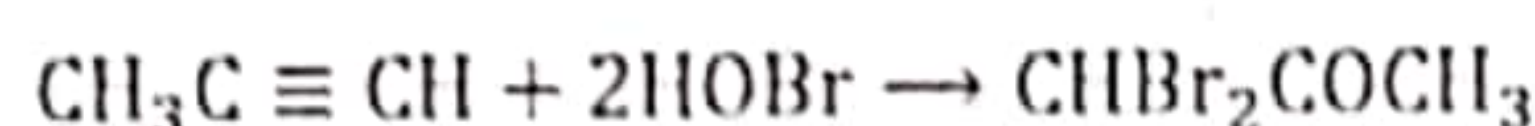
Generally;



Examples



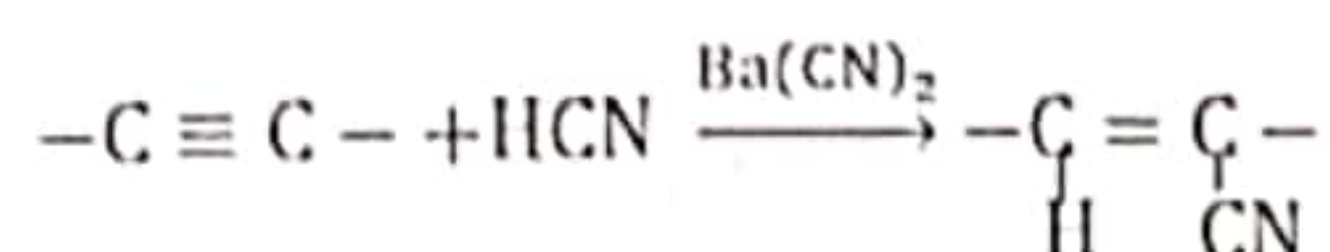
Similarly;



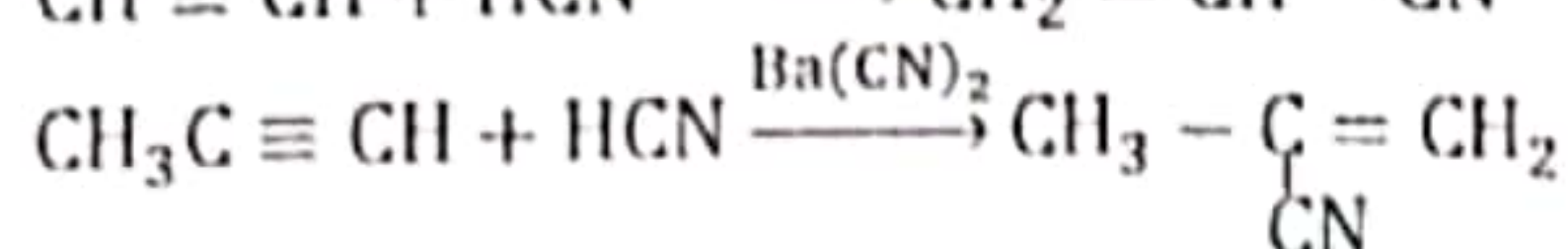
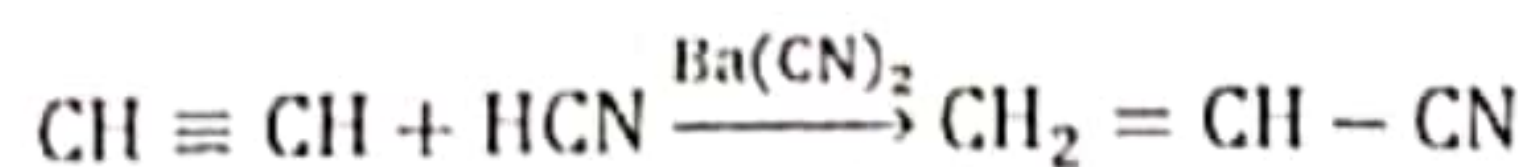
Addition of HCN

Alkyne reacts with hydrogen cyanide under presence of barium cyanide to give unsaturated nitrile with $\text{C} = \text{C}$ (HCN cause cleavage of one π only).

Generally;



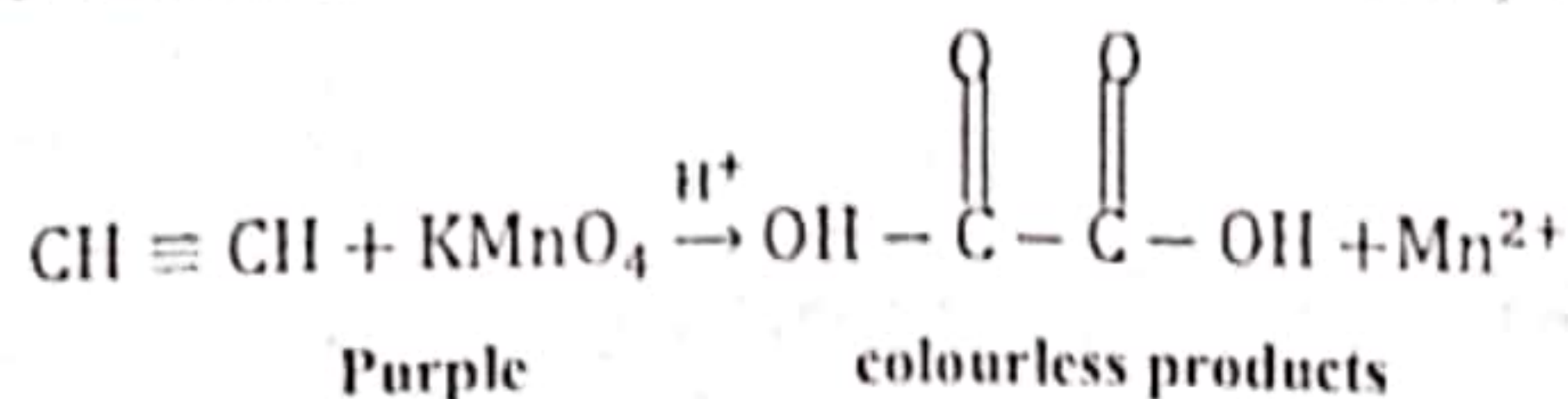
For example;



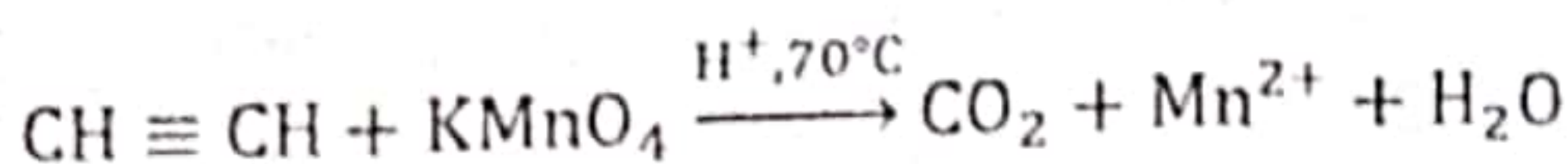
Reaction with acidified Potassium Permanganate

Alkynes decolourise acidified potassium permanganate yielding dicarboxylic acid or monocarboxylic acid. Thus like alkenes, they give positive Baeyer test.

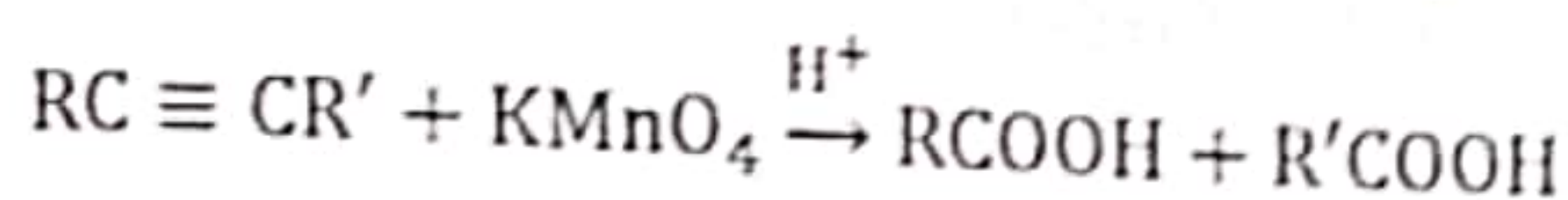
- Ethyne gives ethanedioic acid (common name: oxalic acid) which is dicarboxylic acid.



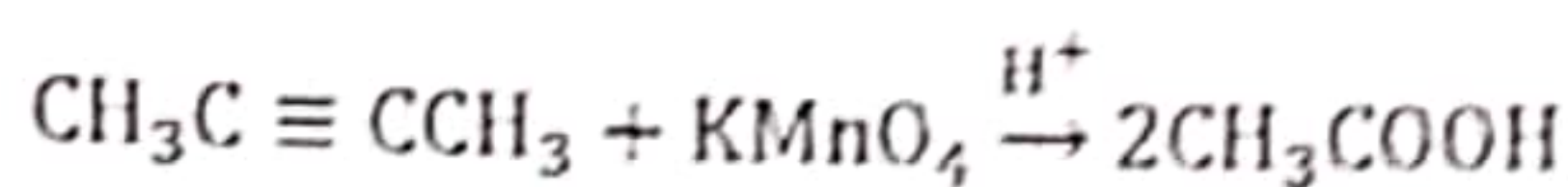
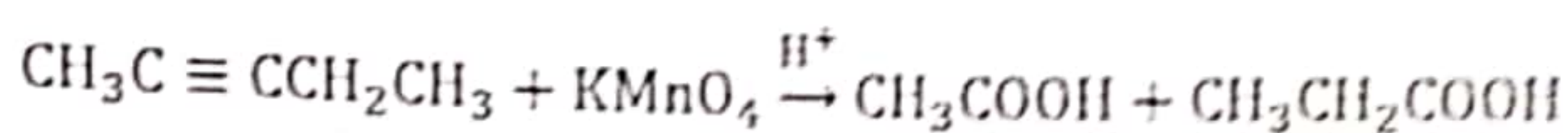
At 70°C , the oxalic acid undergoes further oxidation to give CO_2 . The oxidation of oxalic acid (commonly written as $\text{H}_2\text{C}_2\text{O}_4$) by acidified potassium permanganate is very useful reaction in quantitative analysis through redox titration.



- For other alkynes, triple bond breaks to give monocarboxylic acid.



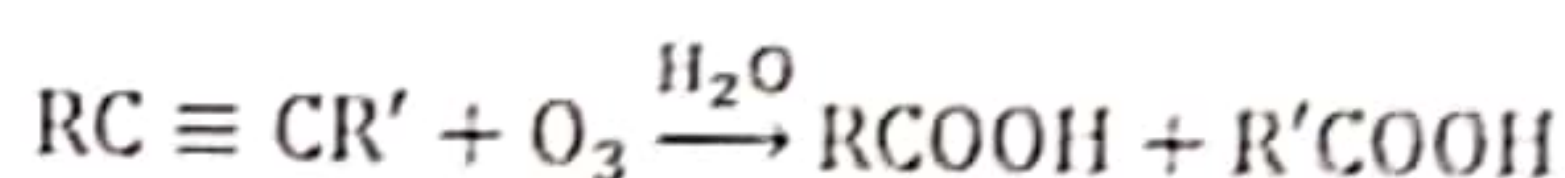
For example;



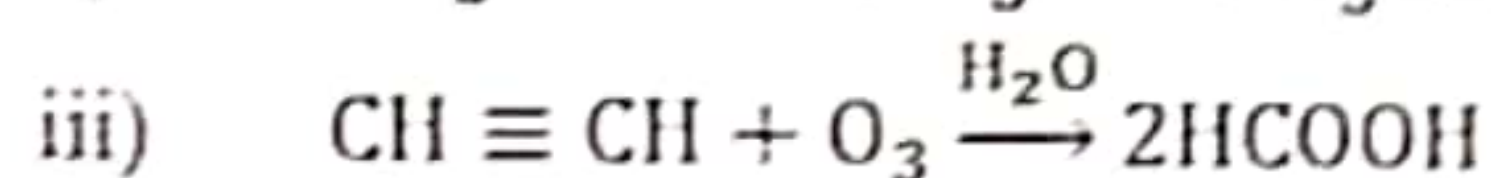
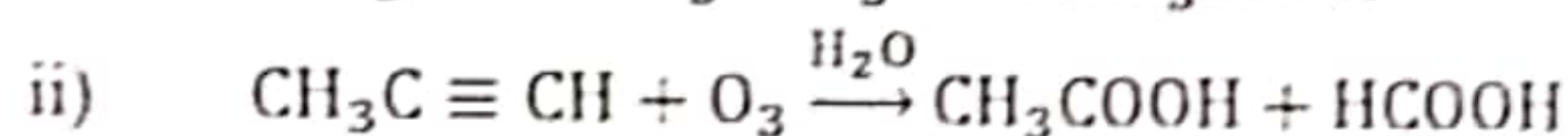
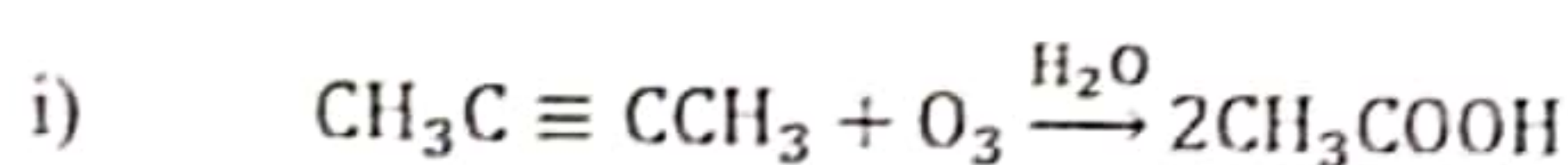
Reaction with ozone under presence of water

Alkynes react with ozone under presence of water yielding carboxylic acids.

Generally;



Examples:



In (ii) and (iii) above if ozone present in excess, methanoic acid (HCOOH) can undergo further oxidation yielding CO_2 and H_2O .

- Also products formed in the above reaction can be used to determine the position of $C \equiv C$ in the alkyne.

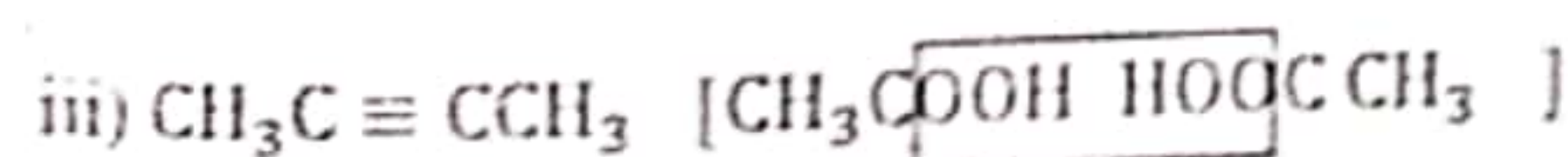
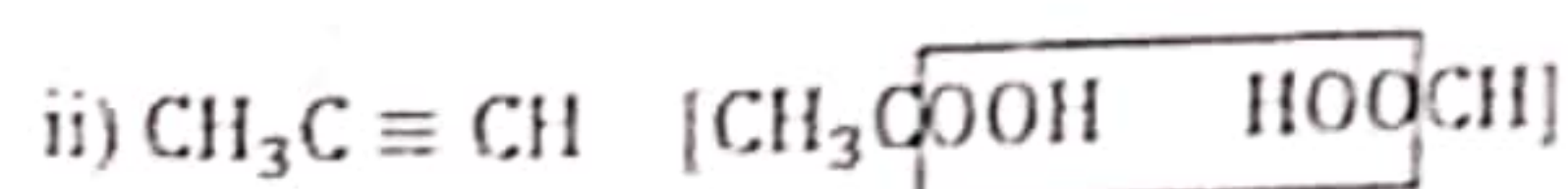
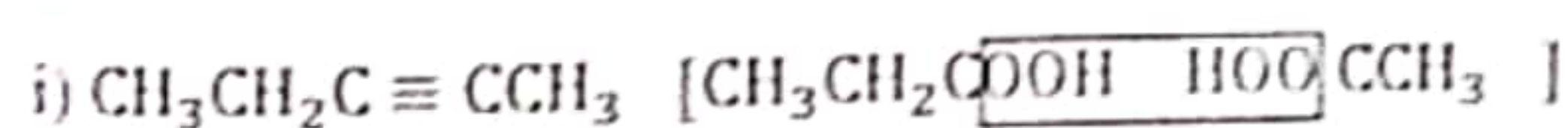
Example 36

Write structure of alkynes which give the following products on ozonolysis;

i) CH_3CH_2COOH and CH_3COOH ii) CH_3COOH and $HCOOH$

iii) $2CH_3COOH$

Solution



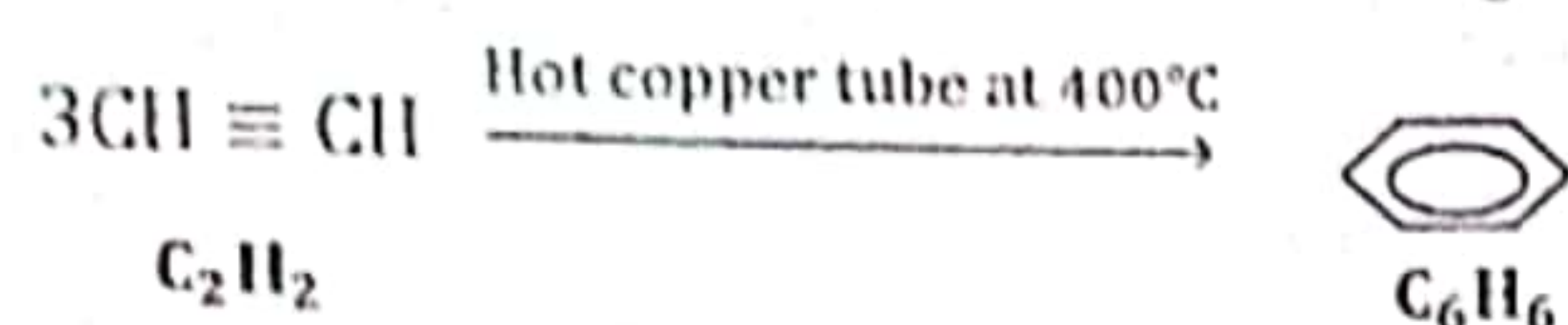
Combustion

Like alkanes and alkenes, alkynes tend to burn in oxygen yielding carbondioxide gas and water on complete combustion. For example; $2CH \equiv CH + 5CO_2 \rightarrow 4CO_2 + 2H_2O$

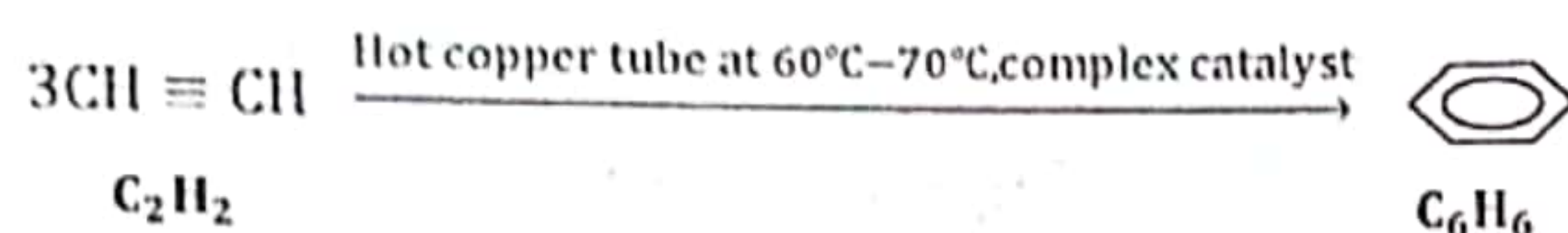
Compared to alkanes and alkenes, alkynes having lowest H:C ratio, have most inefficient combustion giving a heavy smoky luminous flame accompanied with black soot. This is the reasons why alkynes are not commonly used as fuels like alkanes.

Trimerisation

In hot copper tube ethyne trimerises to give benzene.



If the complex catalyst is used the reaction takes place at $60^\circ\text{C} - 70^\circ\text{C}$.



Reactions of alkynes with terminal triple bond

Terminal triple bonded alkyne is the alkyne with triple bond at the first carbon.

- They have the following general structure: $\text{R} \equiv \text{CH}$

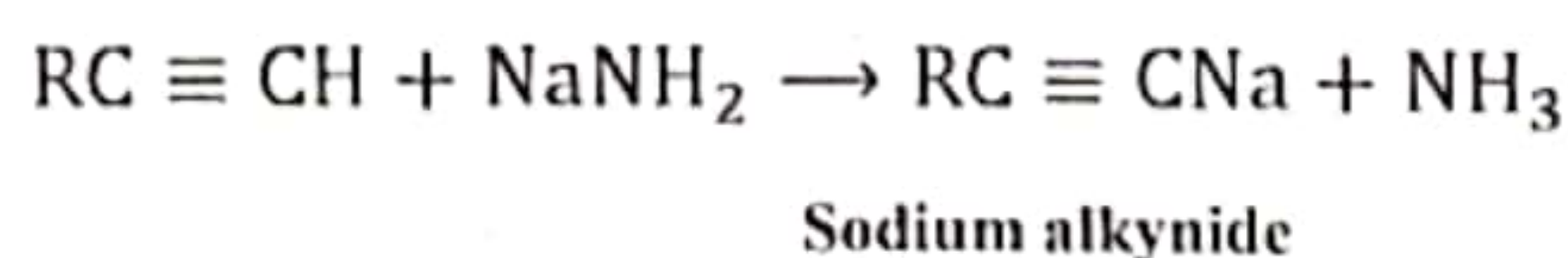
Alkynes with terminal triple bond contain acidic hydrogen in $-\text{C} \equiv \text{CH}$ which can be replaced by strong electropositive metals.

- Below are some reactions which justify the acidic character of hydrogen in the terminal triple bond.

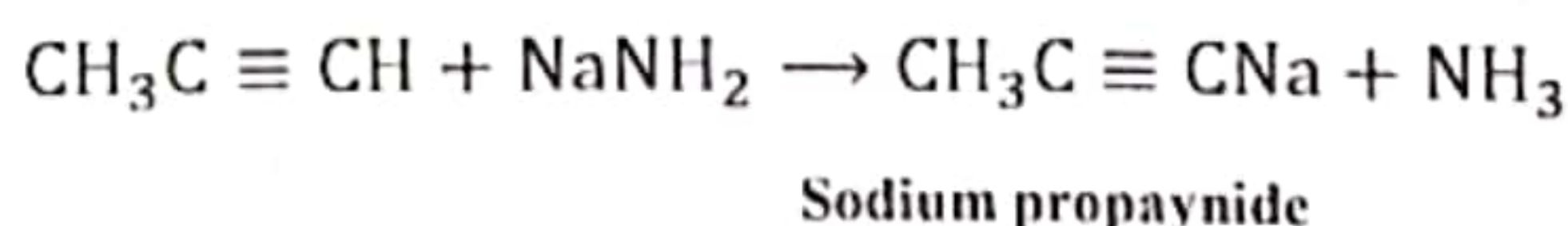
Reaction with Sodium salts (sodium amide)

Alkynes with terminal triple bond react with sodium salts like sodium amide yielding sodium alkynide and ammonia gas is evolved (the gas recognised by its choking smell).

Generally;

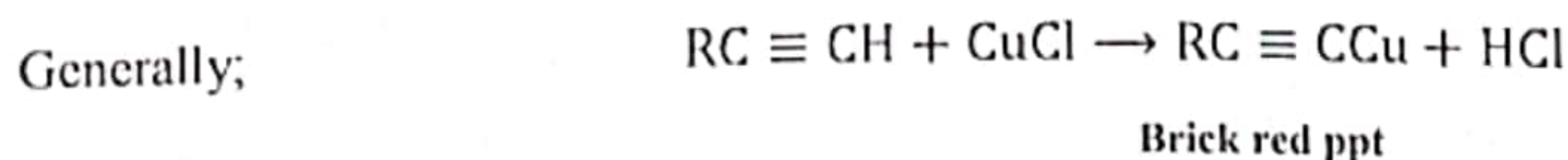


Example;

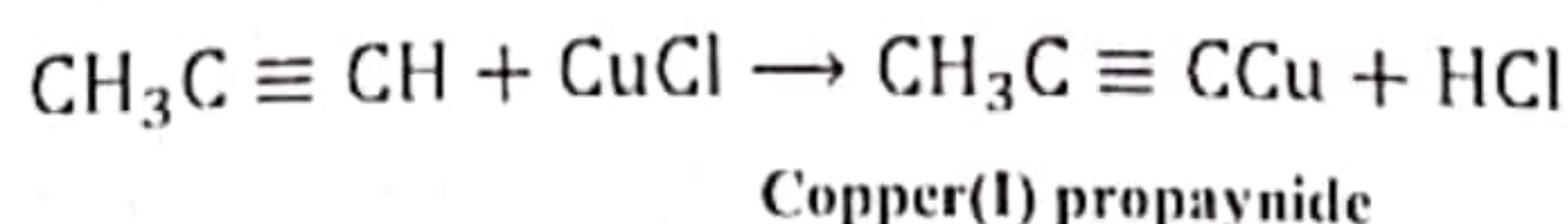


Reaction with copper (I) salts

Alkynes with terminal triple bond reacts with copper (I) salts like Copper (I) chloride yielding Copper (I) alkynide which appears in **brick red colouration**.



Example;

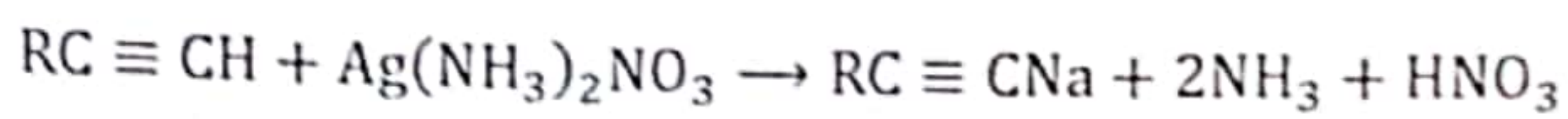


The formation of brick red precipitate in the above reaction gives a test of presence of terminal triple bond in the alkyne.

Reaction with ammonical silver salts

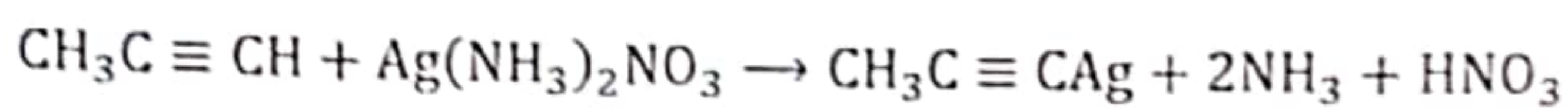
Alkyne with terminal triple bond reacts with ammonical silver salts like ammonical silver nitrate ($\text{Ag}(\text{NH}_3)_2\text{NO}_3$) to give silver alkynide which appears as white precipitate.

Generally;



White ppt

Example



White ppt

Formation of white ppt in the above reaction gives another test of presence of terminal triple bond in alkyne.

Question

Give chemical tests to distinguish the following pairs of organic compounds:

- i) But-2-yne and but -1-yne (2 tests)
- ii) Ethyne and ethene (3 tests)

PRACTICE EXERCISE 12

Problem 1

The following names are incorrect according to rules of IUPAC nomenclature. Draw the structure of each compound and hence give the correct IUPAC name.

- i. 2-methylpent-4-yne
- ii. 4-methyl-3propylpent-1-yne
- iii. 4-isopropylhex-2-yne
- iv. 3,6-heptadiyne
- v. 4-(3-butynyl)octa-1,5-diyne
- vi. 1-buten-3-yne

Problem 2

Write chemical equations to show preparation of the following compounds

- i. Vinyl chloride from 1,2-dichloroethane
- ii. Pent-2-yne from propyne
- iii. Ethyne from chloroform
- iv. Ethyne from coke
- v. Acetylene from ethylene

Problem 3

Account for the following facts:

- i. Hydro bromination of ethyne give 1,1-dibromoethane and not 1,2-dibromoethane
- ii. Hydrogenation of ethyne under presence of palladium catalyst in barium sulphate gives ethene and not ethane.
- iii. Iodination of but-2-yne gives 2,3-diiodobut-2-ene and not 2,2,3,3-tetraiodobutane
- iv. But-1-yne reacts with ammonical silver (I) hydroxide while but-2-yne does not
- v. Ethyne gives effervescence of colourless gas with not acidified KMnO_4 while but-2-yne does not.

Problem 4

Complete the following organic reactions:

- i. $\text{CH}_3\text{C} \equiv \text{CH} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4, 60^\circ\text{C}}$
- ii. $\text{CH}_3\text{C} \equiv \text{CH} + \text{HCN} \xrightarrow{\text{Ba}(\text{CN})_2}$
- iii. Ethyne $\xrightarrow{\text{Trimerisation}}$
- iv. $\text{CH}_3\text{C} \equiv \text{CH} + \text{Cu}(\text{NH}_3)_2\text{OH} \rightarrow$
- v. $\text{CH} \equiv \text{CH} + \text{Excess Cu}(\text{NH}_3)_2\text{NO}_3 \rightarrow$

PART THREE

AROMATIC HYDROCARBBONS

Chapter 13 BENZENE

Benzene is cyclic unsaturated hydrocarbon with molecular formula of C_6H_6 .

- It is highly unsaturated molecule but it does not undergo addition reaction readily and it tends to undergo substitution reactions instead.

Benzene is the basic component of class of organic compounds called aromatic compounds (literally 'aroma' means 'sweet smell', the physical property shown by benzene).

- It is naturally found in the crude oil.

STRUCTURE OF BENZENE

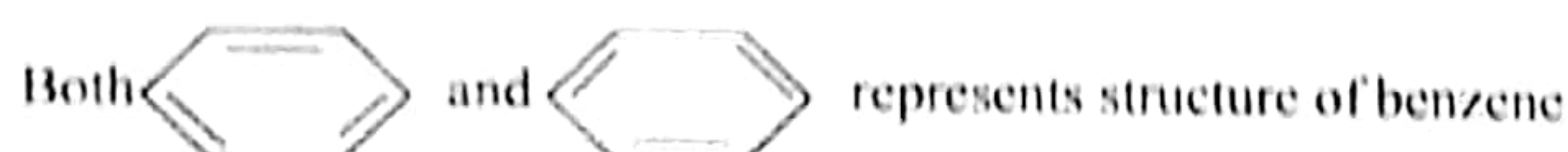
Structure of benzene can be expressed by using

- Kekule structure or
- Resonance structure

Kekule structure

According to Kekule,

- Structure of benzene is hexagonal (it is cyclic structure with six carbon atoms).
- In the structure of benzene carbon-carbon double bond alternates with carbon-carbon single bond.
- The structure of benzene is interconvertible. That is;



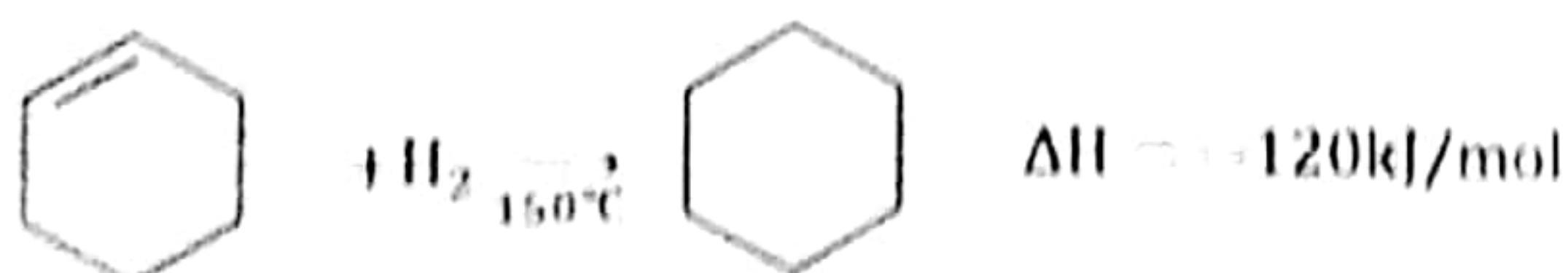
Strength of Kekule structure

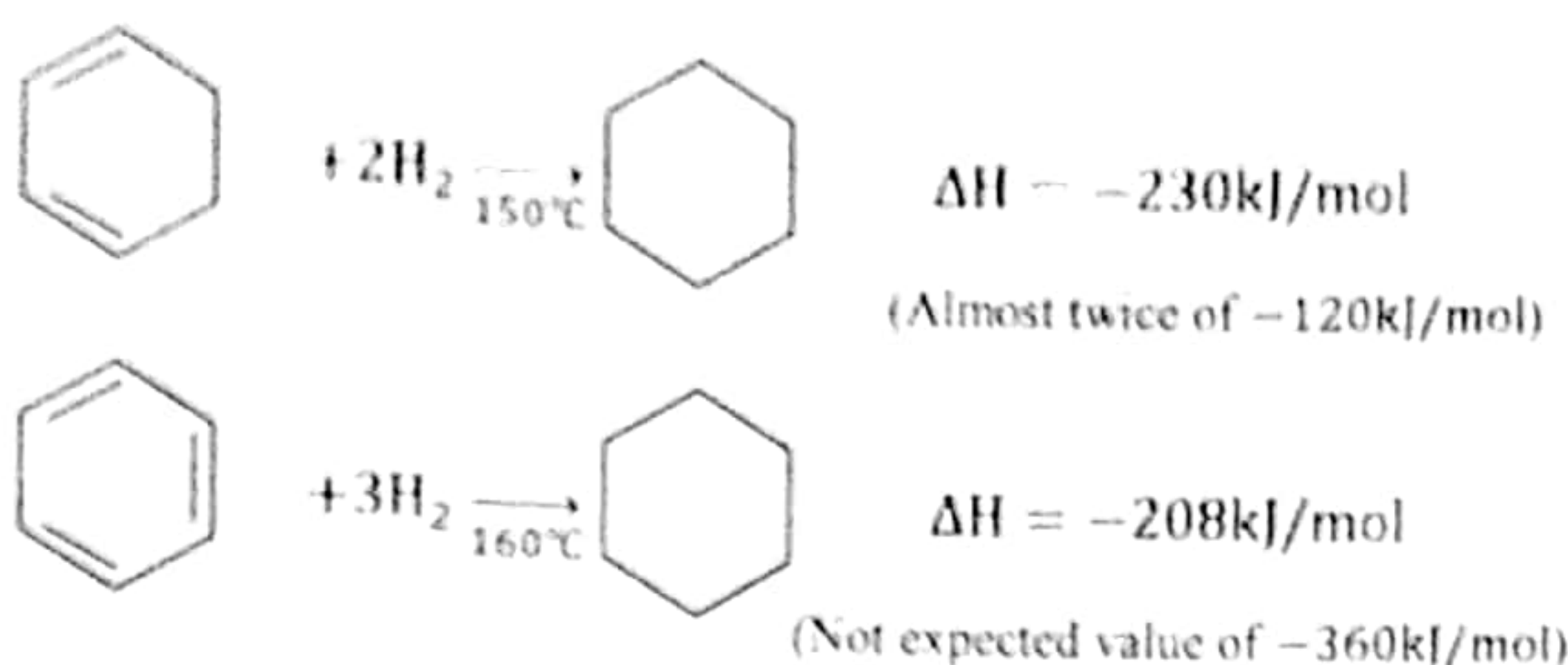
- It gives correct molecular formula of benzene which is C_6H_6
- It is true that all C-H bonds are identical throughout the benzene.

Weakness of Kekule structure

- It fails to explain why benzene does not undergo addition reaction readily and it tends to undergo substitution reactions instead.
- Through x-ray diffraction it can be seen that carbon-carbon bond lengths are equal throughout the benzene, the fact which cannot be explained by Kekulé structure (According to Kekulé structure there is $C \equiv C$ and $C-C$ so it was expected that bond length of $C \equiv C$ to be shorter than that of $C-C$).
- It does not explain low experimental value of heat of hydrogenation of benzene.

That is:





Resonance structure

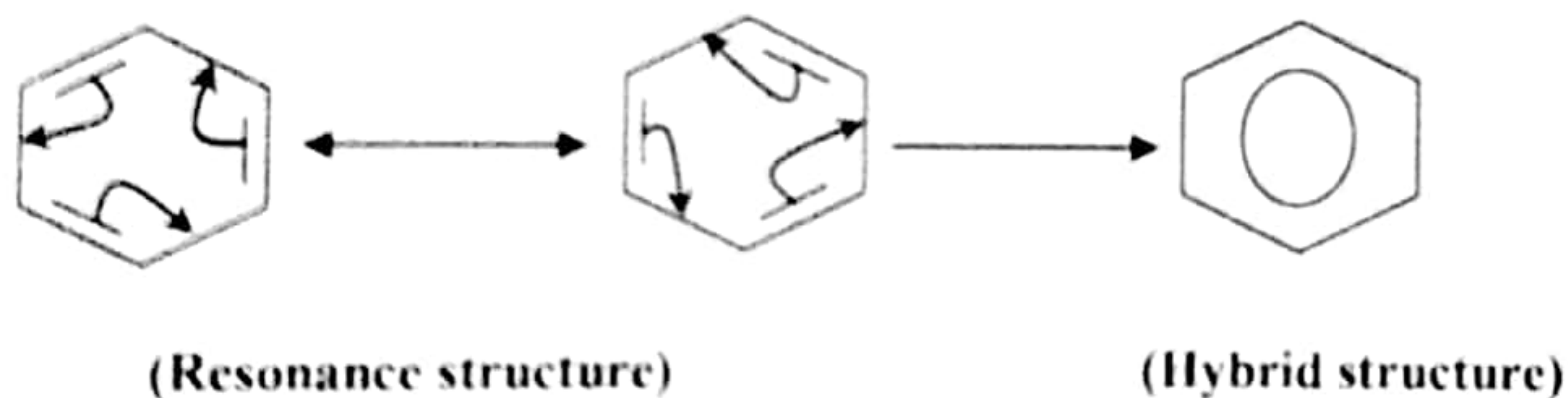
According to resonance theory:

- Neither of the two structure of benzene given by Kekule gives proper representation of the structure of benzene.
- The correct structure of benzene is the hybrid of the two structures given by Kekule.

Thus the structure of benzene is,



The structure of benzene given by resonance theory comes from the fact that; alternation of $\text{C}=\text{C}$ and $\text{C}-\text{C}$ in benzene favours occurrence of mesomerism in benzene, that is π -electrons in benzene are not localized instead they are delocalized throughout the benzene as shown below.



Strength of resonance structure

It explains why benzene does not undergo addition reactions readily and it undergoes substitution reaction instead.

Reason:

π -electrons in benzene are involved in mesomerism, i.e. they are not localized.

- So for benzene to undergo addition reaction high amount of energy must be absorbed to stop the resonance before breaking π -bonds so as to add atoms to carbon atoms. This makes more difficult for it to undergo addition reaction and hence it tends to undergo substitution reaction which requires lower amount of energy and therefore substitution reactions are more favoured than addition reactions in case of benzene.

In few words we can say that benzene cannot undergo addition reaction readily although it is highly unsaturated hydrocarbon because its π electrons are stabilised by mesomerism.

It explains why carbon- carbon bond lengths are equal throughout the benzene.

Reason:

Since π electrons in benzene are delocalized, every carbon-carbon bond has sigma (δ) bond and partially π (π) bond throughout the benzene

In other words; there is partially carbon-carbon double bond throughout the benzene and hence carbon-carbon bonds are all alike throughout the benzene which in turn make it to have equal bond lengths.

It gives explanation to obtained low experimental value of heat of hydrogenation in benzene.

Reason:

Hydrogenation of benzene is addition reaction, so extra energy is required (absorbed) to break resonance before doing addition reaction thus reducing net energy which is evolved in the reaction (i.e. reducing heat of hydrogenation). The difference between experimental and expected value amounted to 152kJ/mol is the **resonance energy** (*energy absorbed to break the resonance*) in benzene.

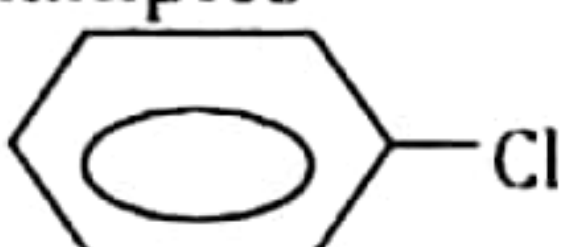
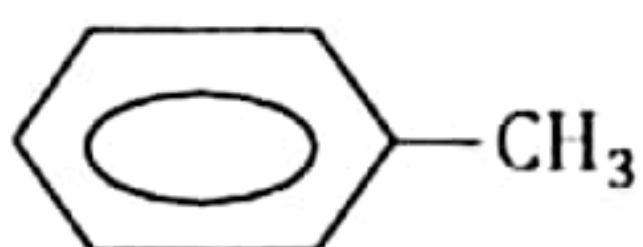
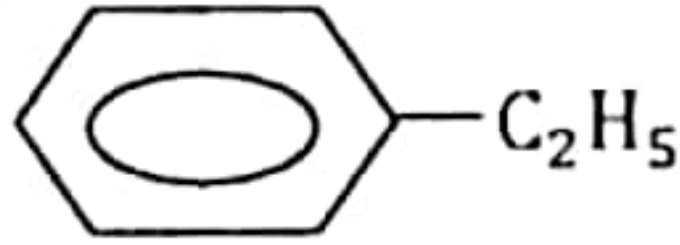
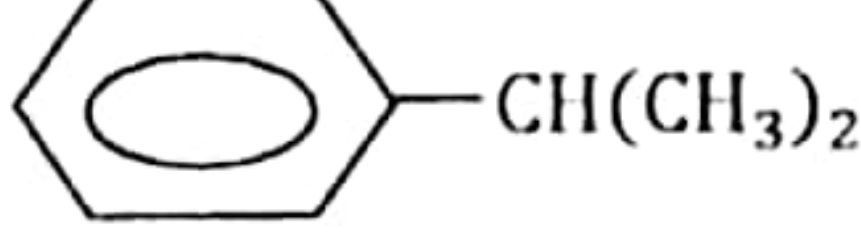
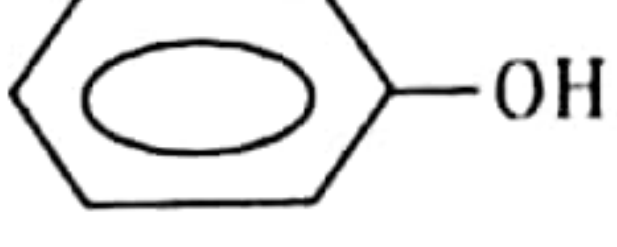
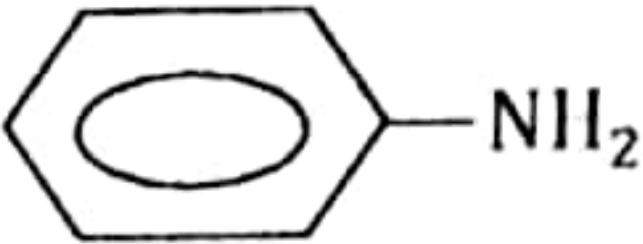
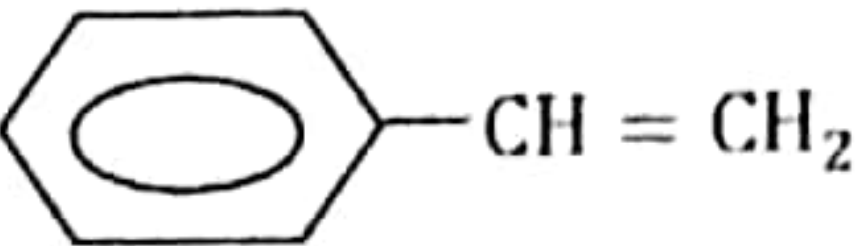
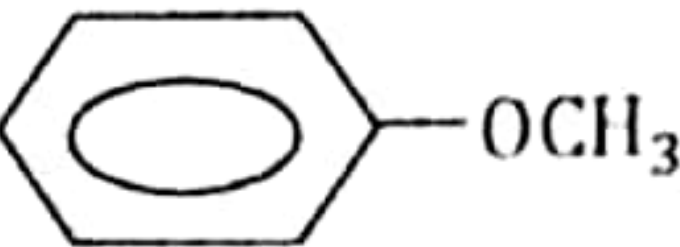
NOMENCLATURE OF COMPOUNDS OF BENZENE

In naming compounds of benzene, the following rules are followed:

Rule 1

Naming of monosubstituted benzene (benzene with only one substituent) is simply done by naming substituent firstly and then end with the word benzene.

Examples

- i)  chlorobenzene
- ii)  methylbenzene (common name: **toluene**)
- iii)  ethylbenzene
- iv)  isopropylbenzene (common name: **cumene**)
- v)  hydroxybenzene (common name: **phenol**)
- vi)  aminobenzene (common name: **aniline**)
- vii)  vinylbenzene (common name: **styrene**)
- viii)  methoxybenzene (common name: **anisole**)

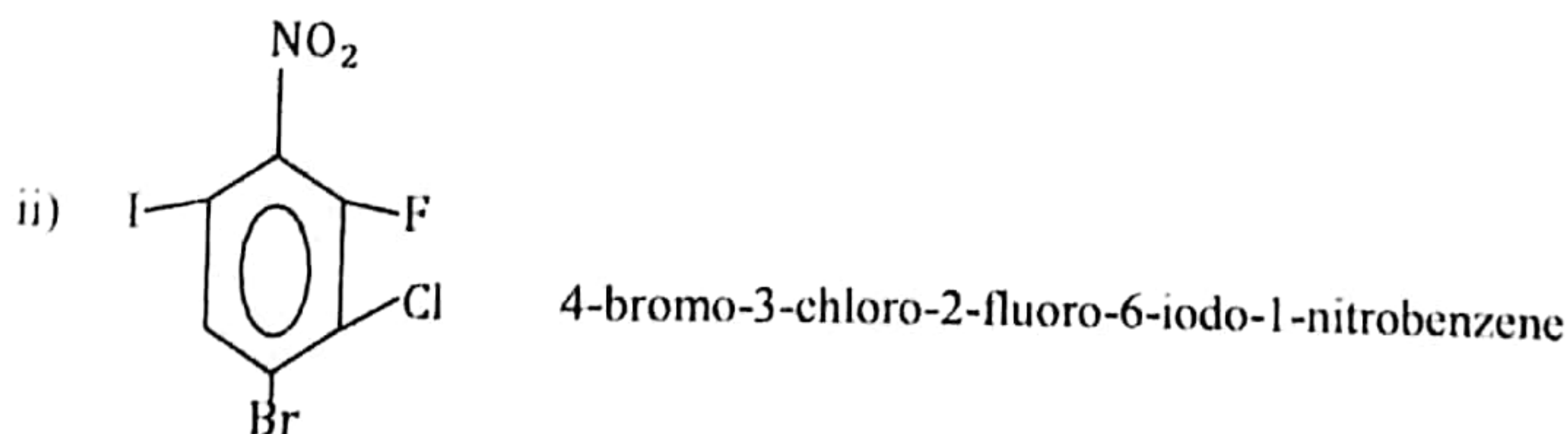
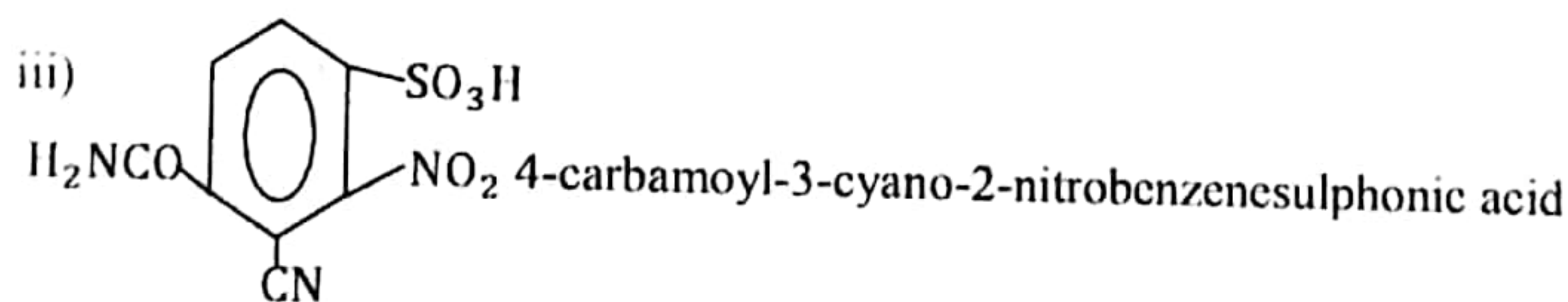
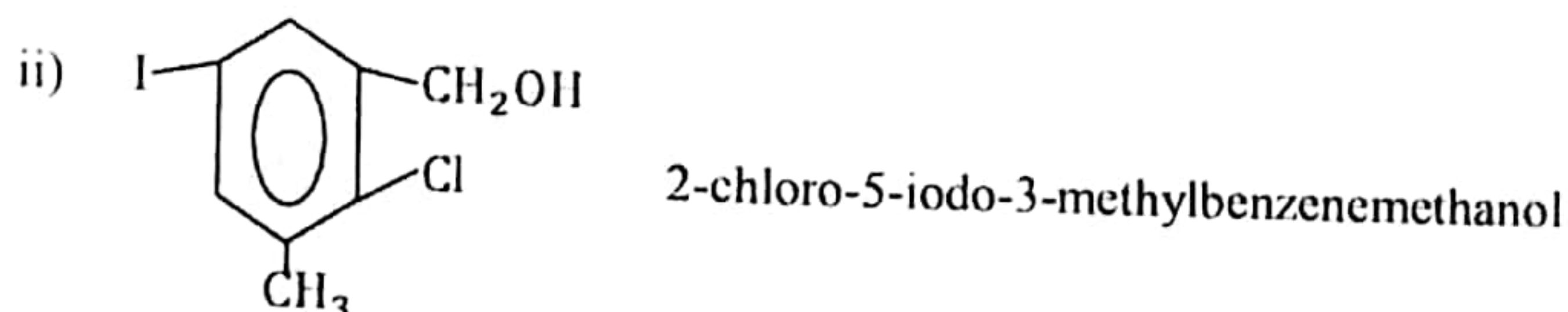
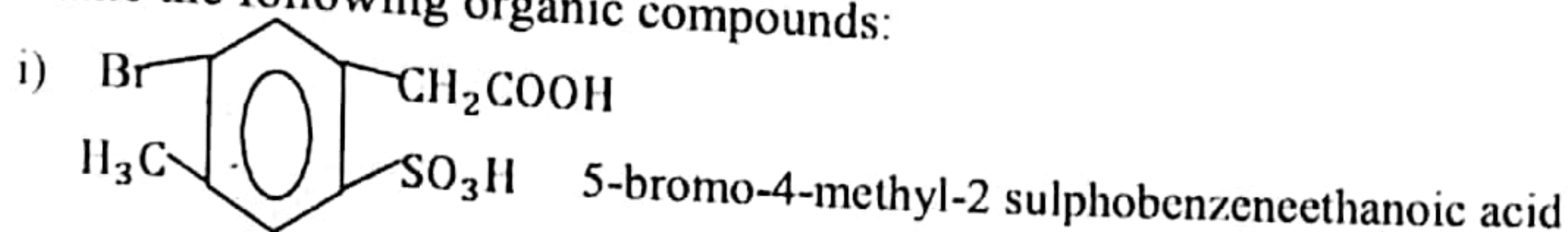
Rule 2

In naming compound of benzene with more than one substituent, the following procedures are followed;

- First determine the most dominant group.
- The preference of choosing dominant group follows the following order:
 $-\text{COOH} > -\text{SO}_3\text{H} > -\text{CONH}_2 > -\text{CN}, -\text{COOR} > -\text{CO}- > -\text{NH}_2, -\text{OH}, \text{R} > -\text{NO}_2, \text{X}$
- In numbering carbon atoms in benzene ring, the carbon with most dominant group must be given first position and then proceed to the direction closer to another substituent (lowest sum rule).
- In naming compound of benzene, starts naming less dominant groups according to their alphabetical order regardless to their dominance then add the word benzene ending with the name of most dominant group.

Example

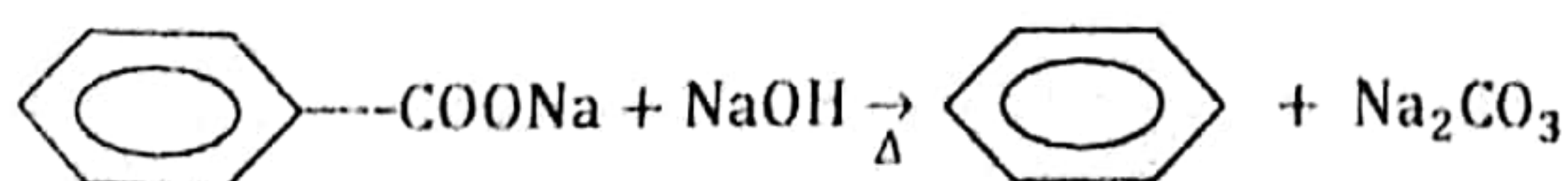
Name the following organic compounds:



PREPARATIONS OF BENZENE

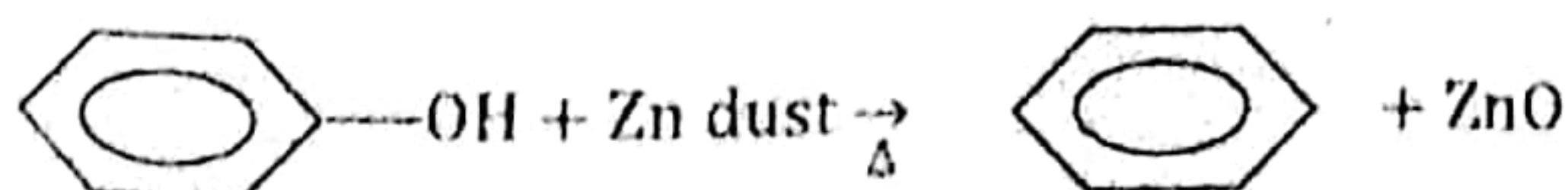
Decarboxylation of benzoic salts

When Sodium benzoate is heated with sodium hydroxide benzene is formed.



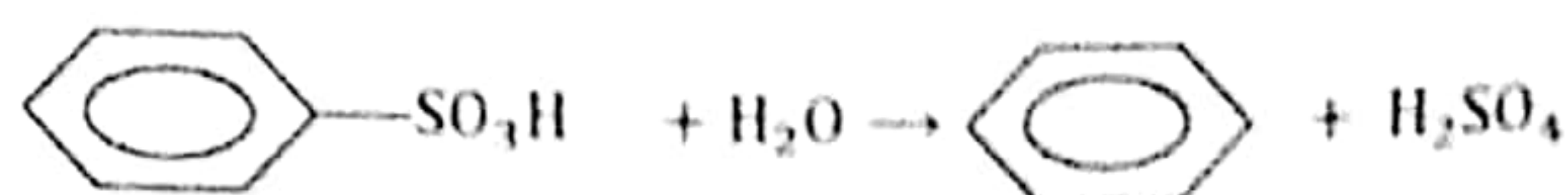
Reaction between phenol and zinc

When phenol is heated with zinc dust, benzene is formed.



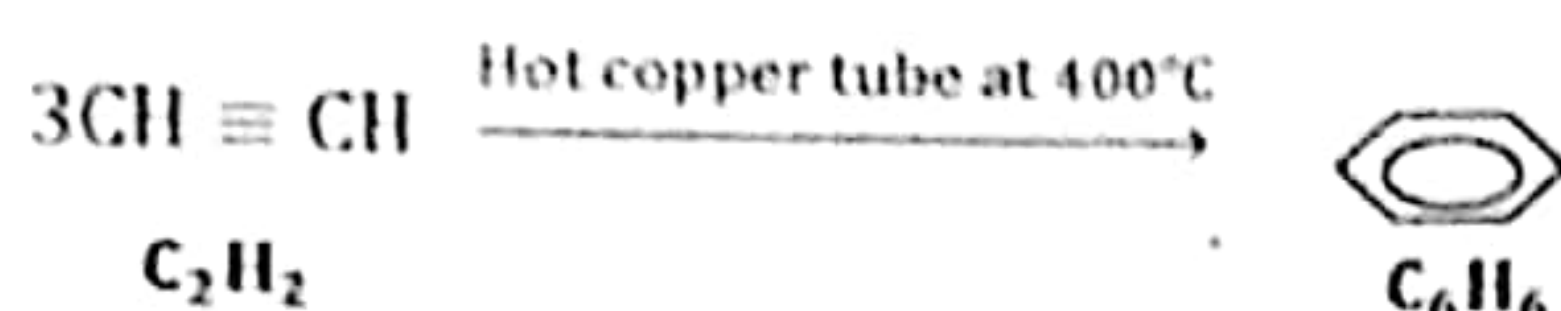
Hydrolysis of sulphobenzene

Sulphobenzene tends to react with water yielding benzene.

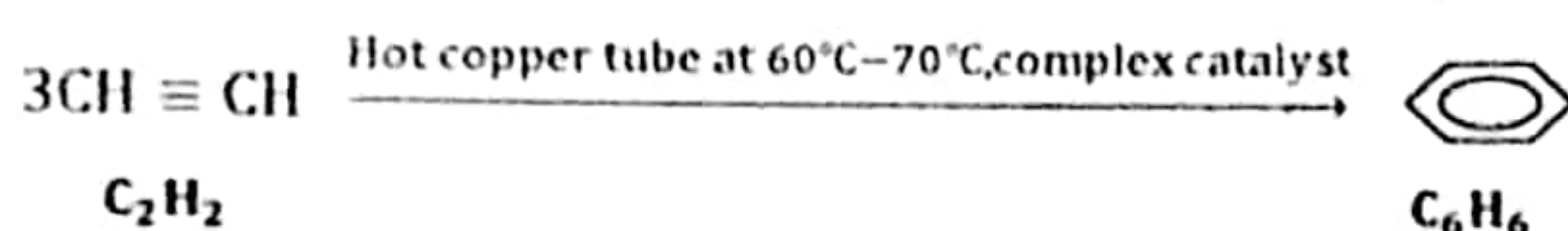


Trimerisation of ethyne

In hot copper tube ethyne trimerises to give benzene.



The employment of such high temperature makes the method undesirable. However if the complex catalyst is used the reaction takes place at milder temperature ($60^\circ\text{C} - 70^\circ\text{C}$).



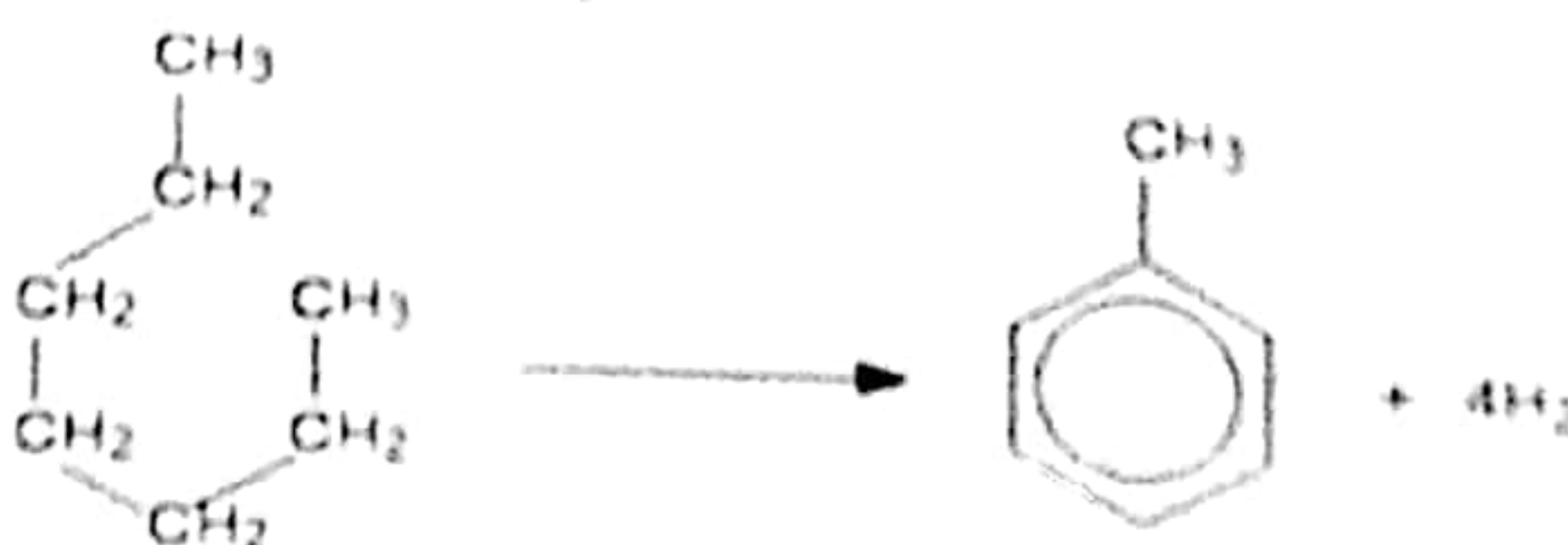
MANUFACTURE OF BENZENE AND ITS SUBSTITUTED HYDROCARBONS

Benzene and its substituted hydrocarbon like methylbenzene (toluene) is commonly manufactured by catalytic reforming of fraction obtained from fractional distillation of crude oil (petroleum)

- Reforming takes straight chain hydrocarbons in the C_6 to C_8 range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings. Hydrogen is produced as a by-product of the reactions.
- To get benzene, hexane, C_6H_{14} , is used whereby the alkane loses hydrogen yielding benzene. To have better understanding on what is happening, considers the hexane bent into a circle as drawn below:



Similarly, methylbenzene is made from heptane:



How the process is carried out?

The process of catalytic reforming as the method of manufacturing arenes is outlined below

The feedstock

The feedstock is a mixture of the naphtha or gasoline fractions and hydrogen. The hydrogen is there to help prevent the formation of carbon by decomposition of the hydrocarbons at the high temperatures used. The carbon would otherwise contaminate the catalyst

The catalyst

A typical catalyst is a mixture of platinum and aluminium oxide. With a platinum catalyst, the process is sometimes described as "platforming".

Temperature and pressure

The temperature is about 500°C, and the pressure is about 20 atmospheres.

PHYSICAL PROPERTIES OF BENZENE

Below are some of physical properties of benzene.

- It is colourless liquid
- It melts at 5°C and boils at 80°C
- It is less dense than water
- Its vapour density is higher than density of air
- It has sweet smell

Note: Benzene is toxic (it causes cancer).

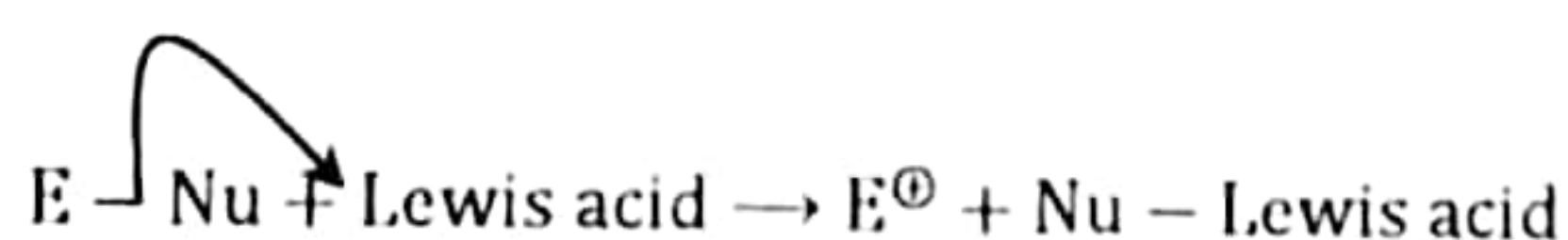
CHEMICAL REACTIONS OF BENZENE

Most of chemical reactions of benzene are electrophilic substitution reactions.

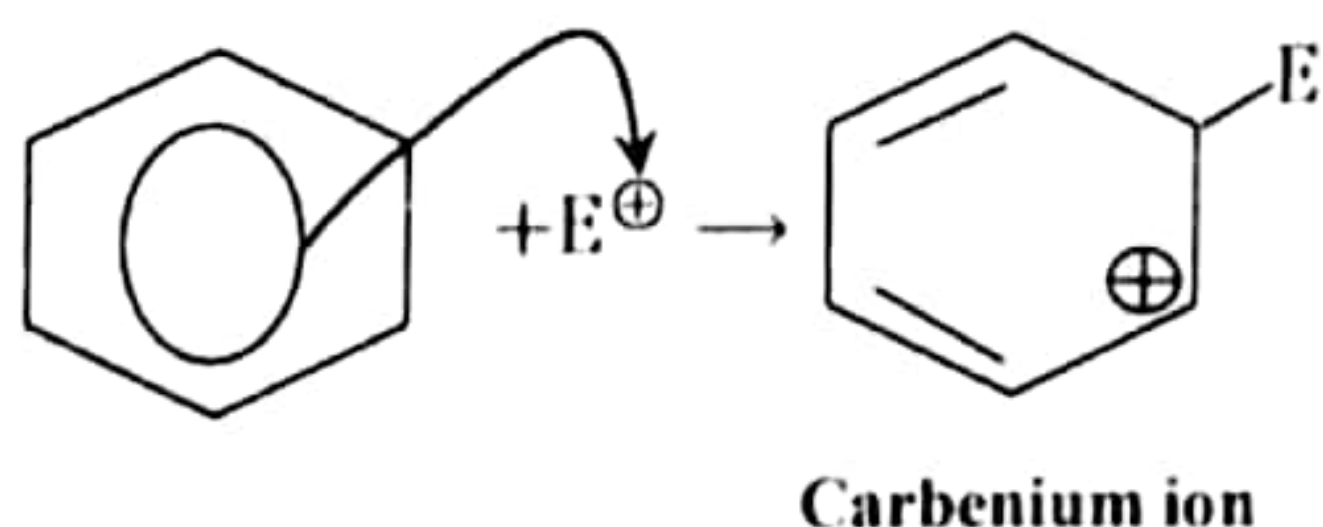
- Electrophilic substitution reactions in benzene occur under presence of lewis acid as catalyst.

Generally, mechanism of electrophilic substitution reaction in benzene follows three steps.

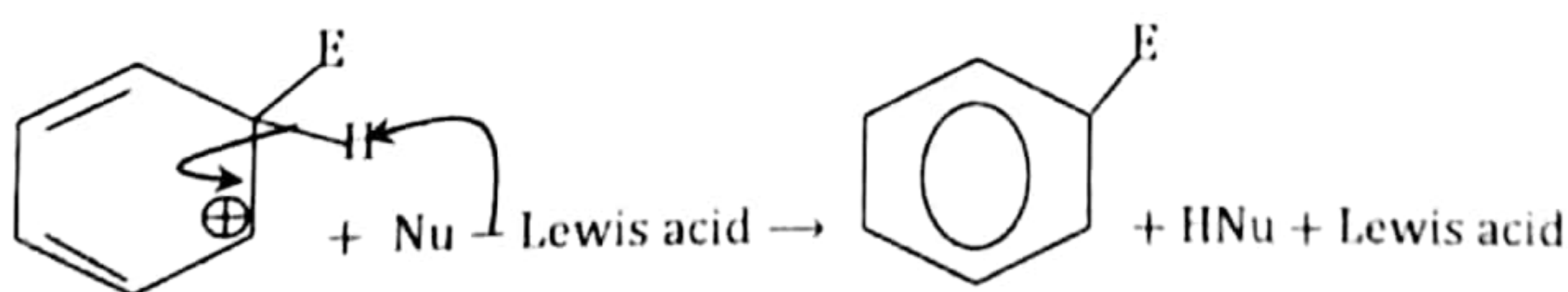
First step: Formation of an electrophile



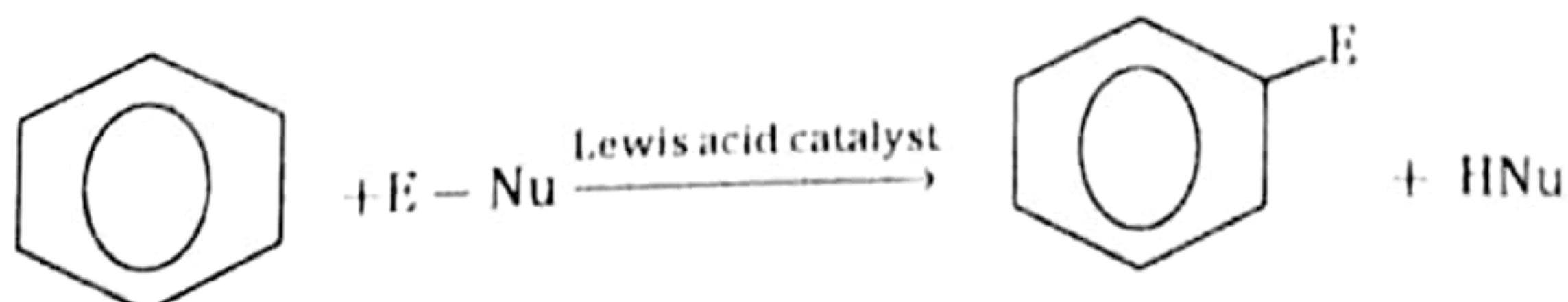
Second step: Formation of intermediate carbenium ion



Thire step: Formation of product and regeneration of catalyst



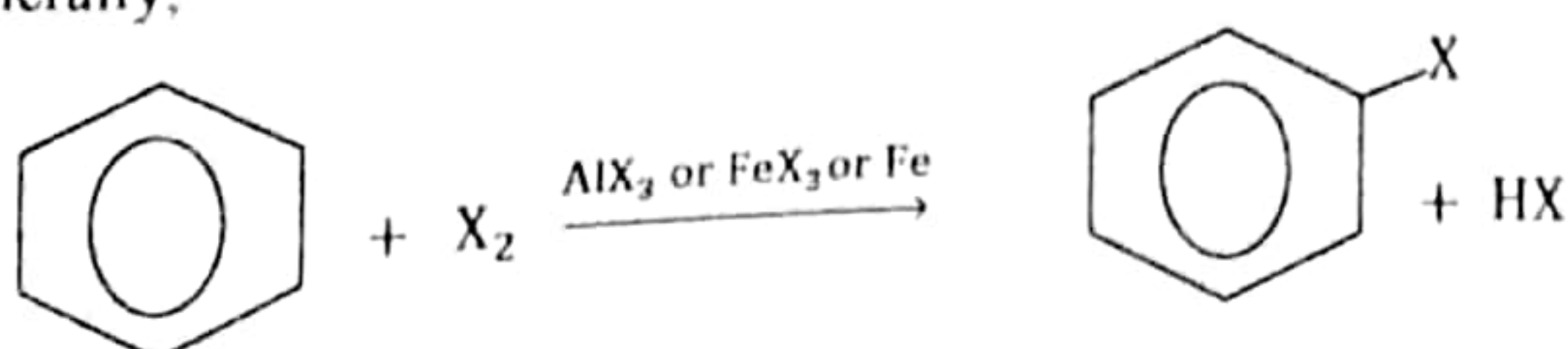
Hence the overall reaction is;



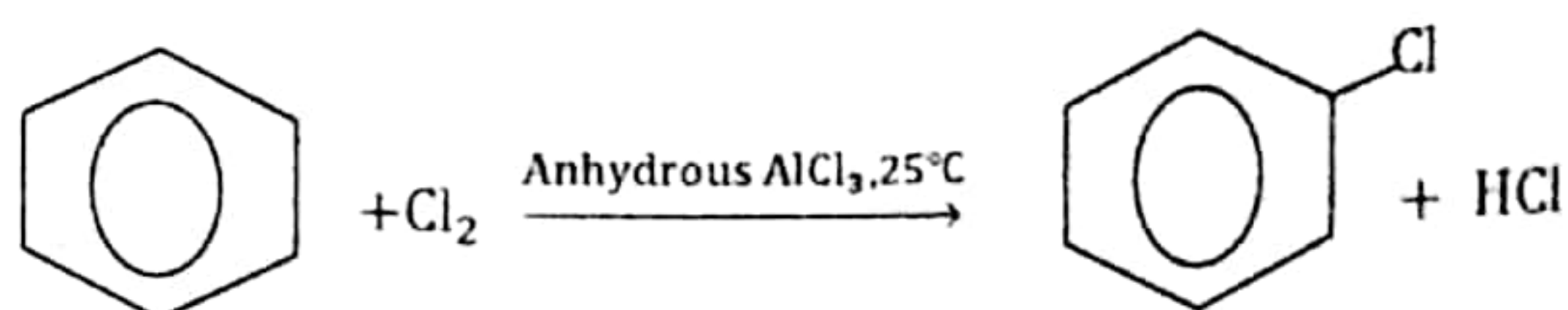
Below are examples of electrophilic substitution reactions in benzene;

Halogenation

Generally;

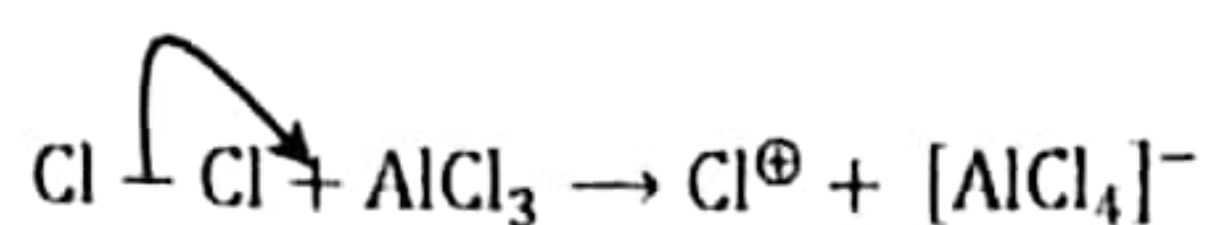


Example;

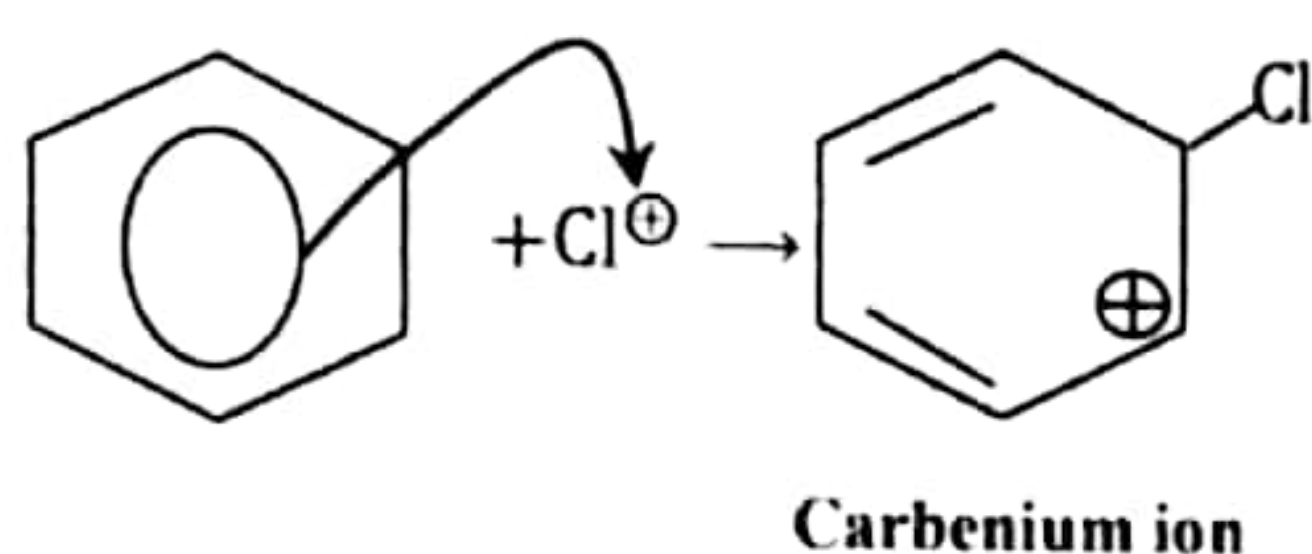


Mechanism:

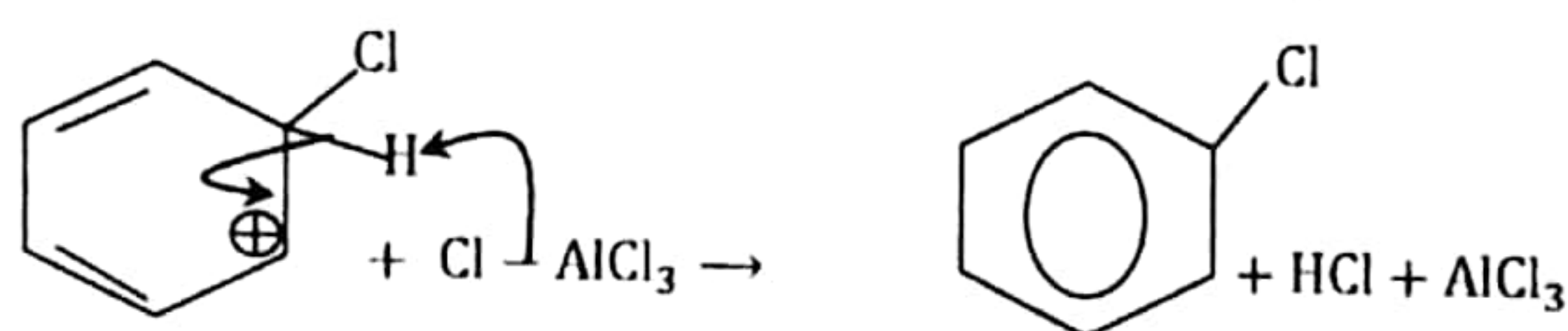
1. Formation of an electrophile



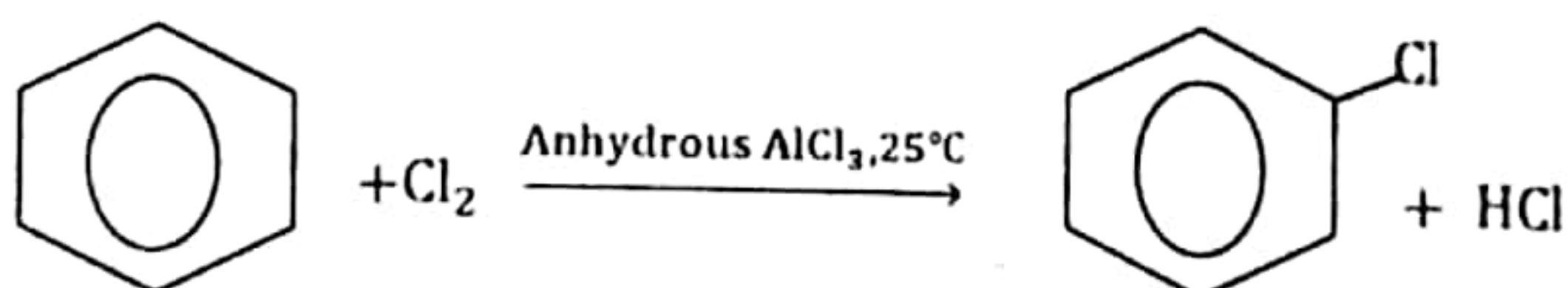
2. Formation of intermediate carbenium ion



3. Formation of product and regeneration of catalyst



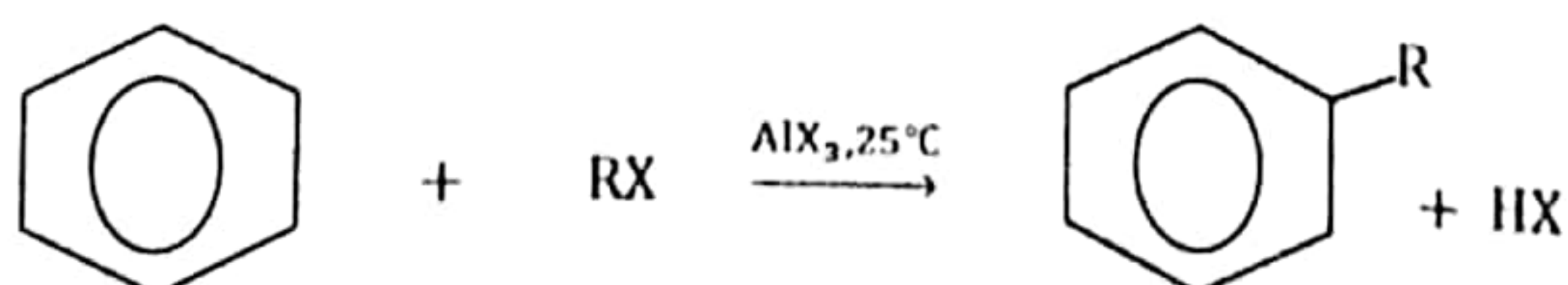
Hence the overall reaction is;



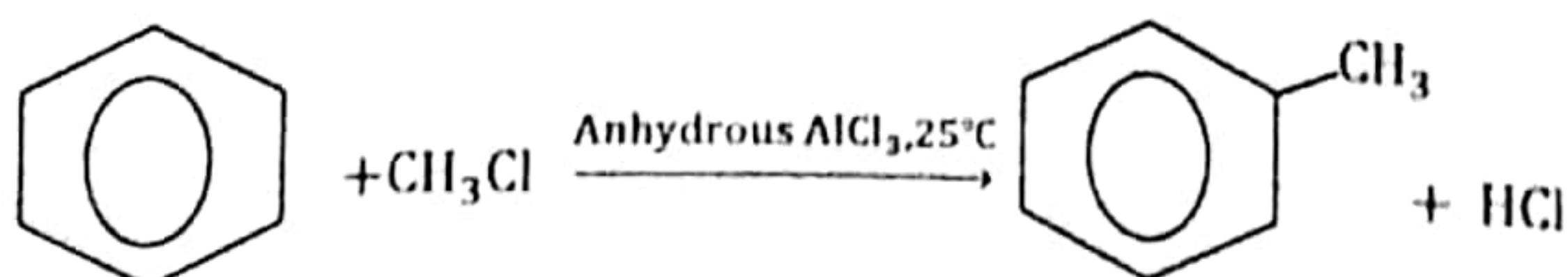
Friedel craft alkylation

Friedel craft alkylation is the electrophilic substitution reaction between benzene and haloalkane under presence of Lewis acid catalyst to give alkylbenzene.

Generally;

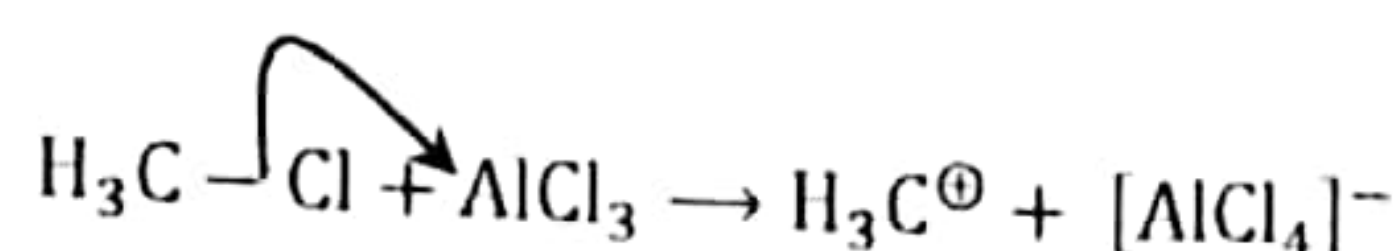


Example;

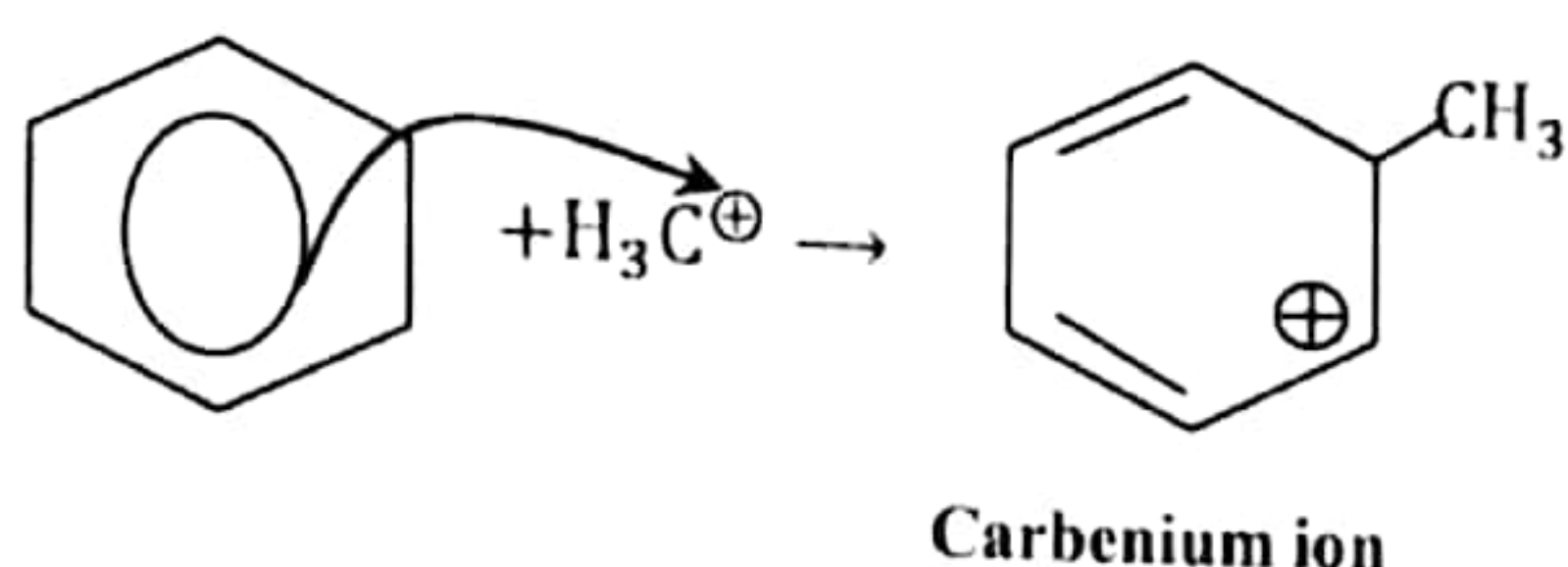


Mechanism:

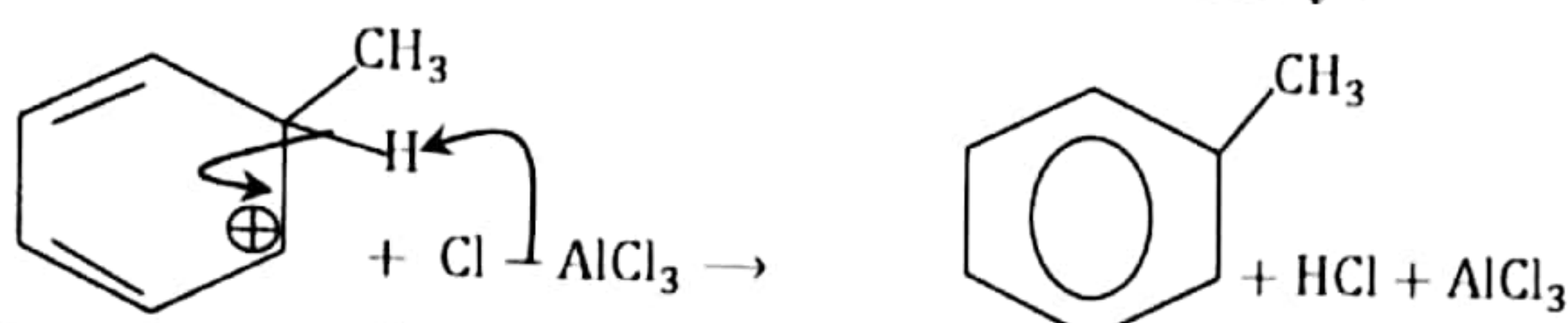
1. Formation of an electrophile



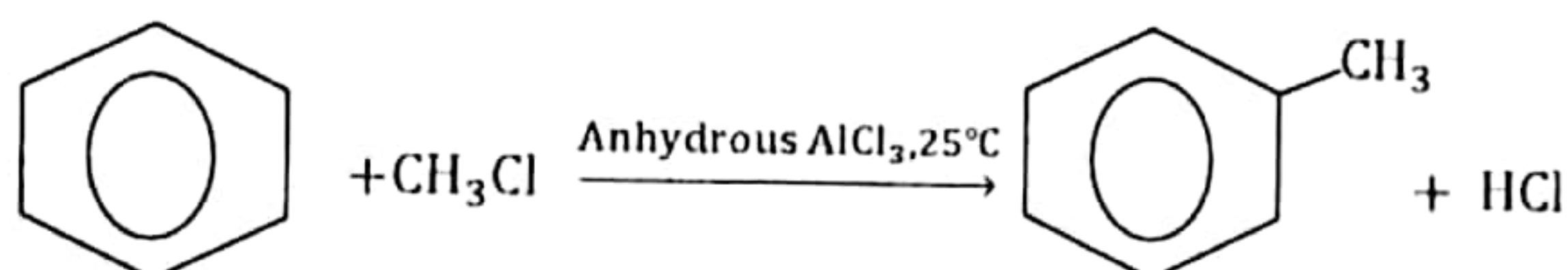
2. Formation of intermediate carbenium ion



3. Formation of product and regeneration of catalyst



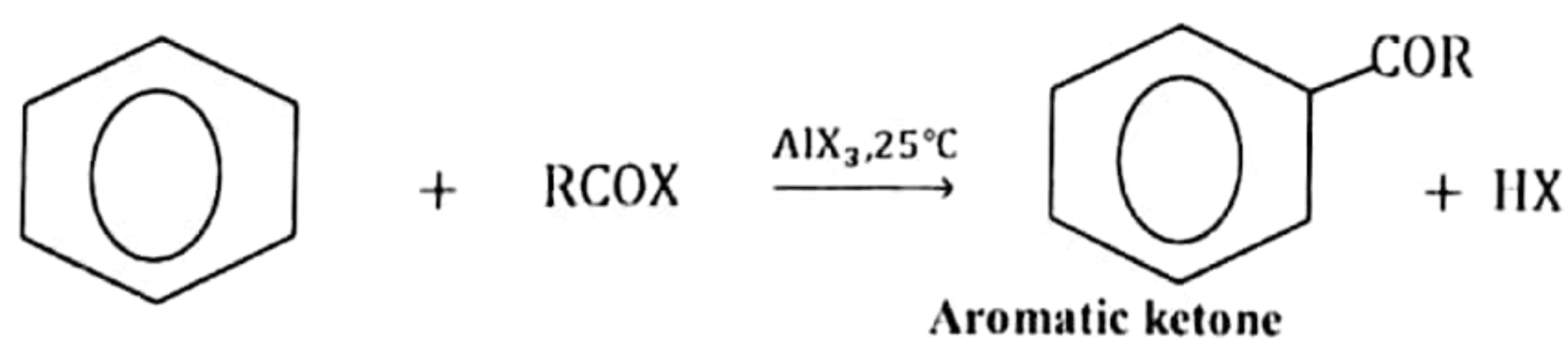
Hence the overall reaction is;



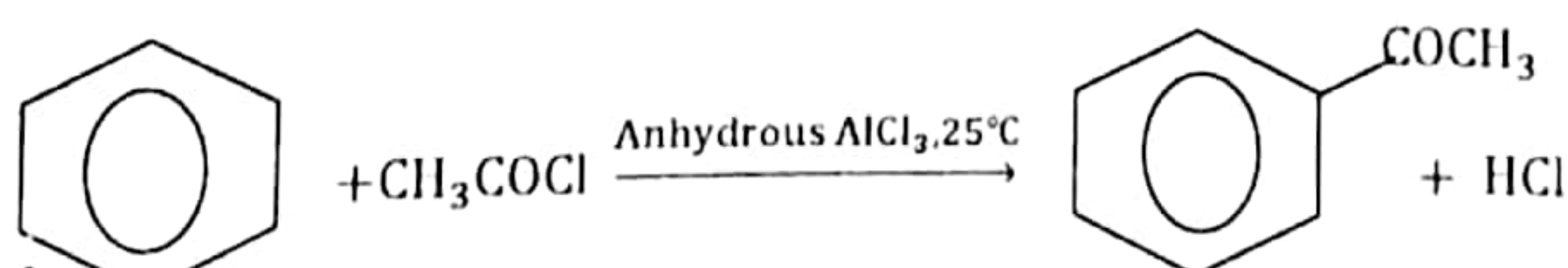
Friedel craft acylation

Friedel craft acylation is the electrophilic substitution reaction between benzene and acyl compounds (acid halide) under presence of Lewis acid catalyst to give aromatic ketone.

Generally;

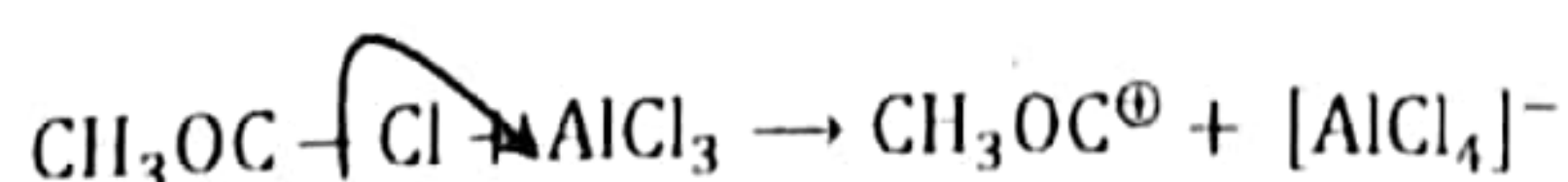


Example;

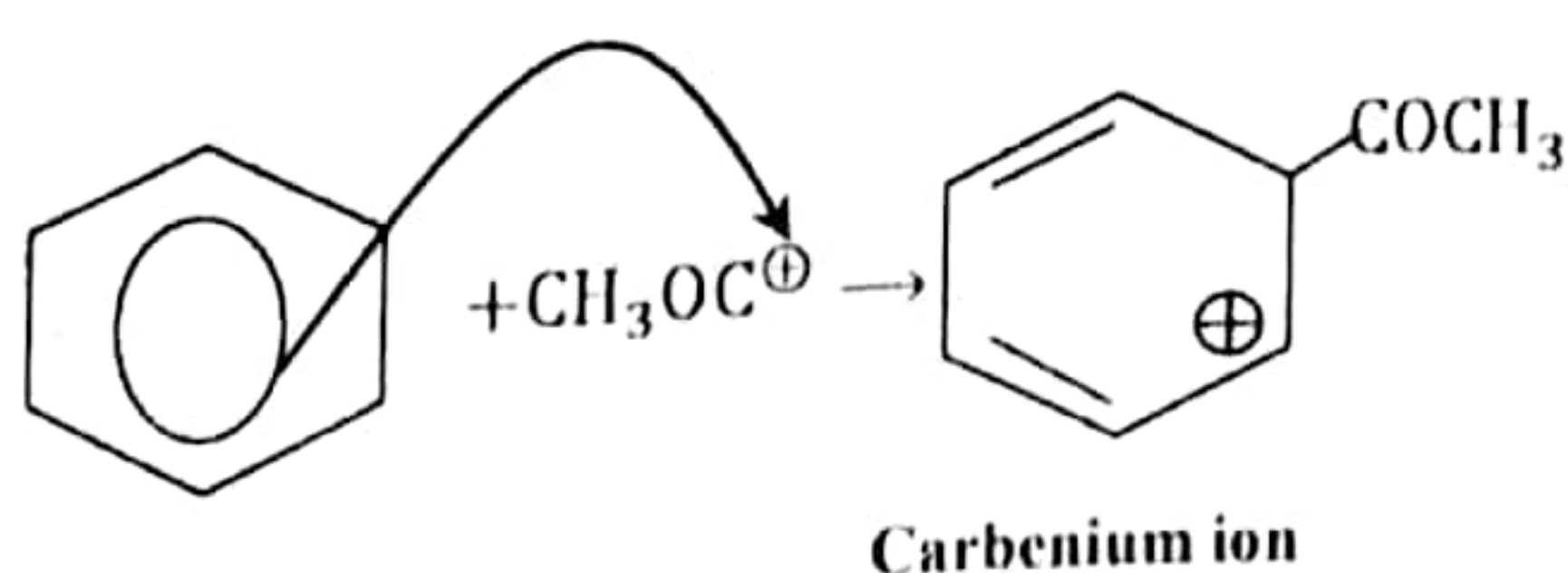


Mechanism:

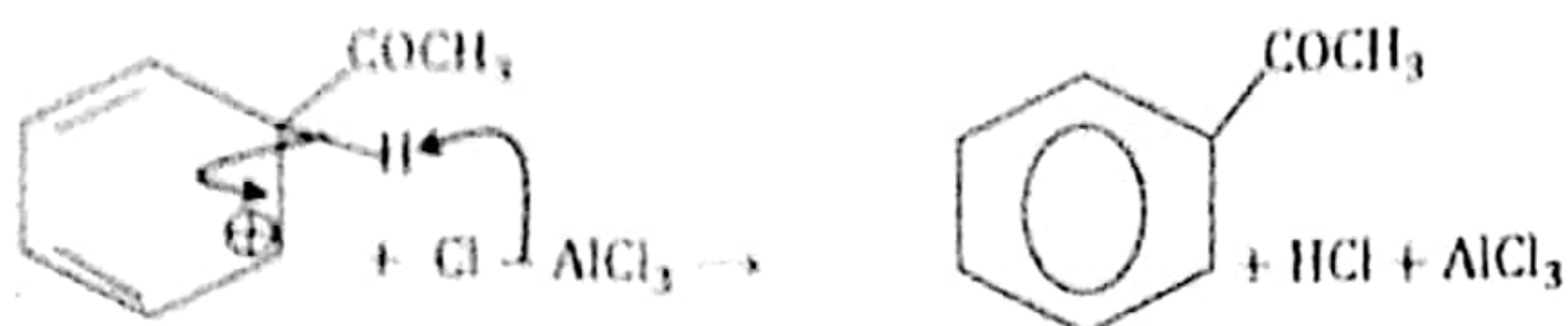
1. Formation of an electrophile



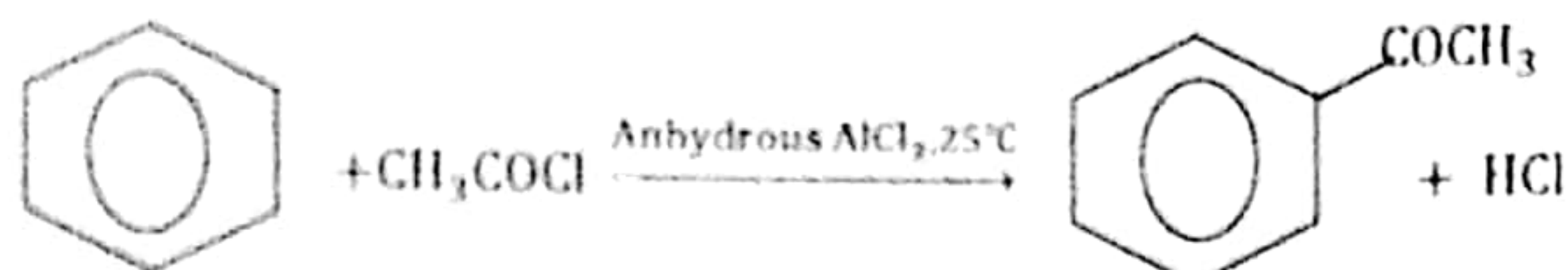
2. Formation of intermediate carbenium ion



3. Formation of product and regeneration of catalyst

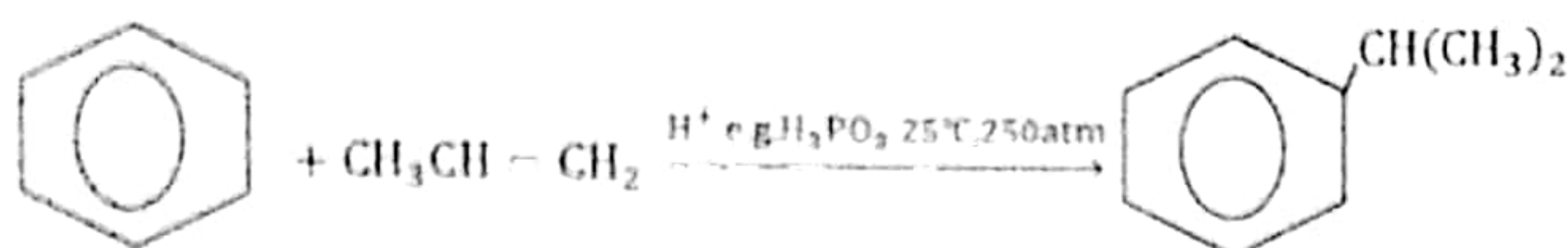


Hence the overall reaction is;



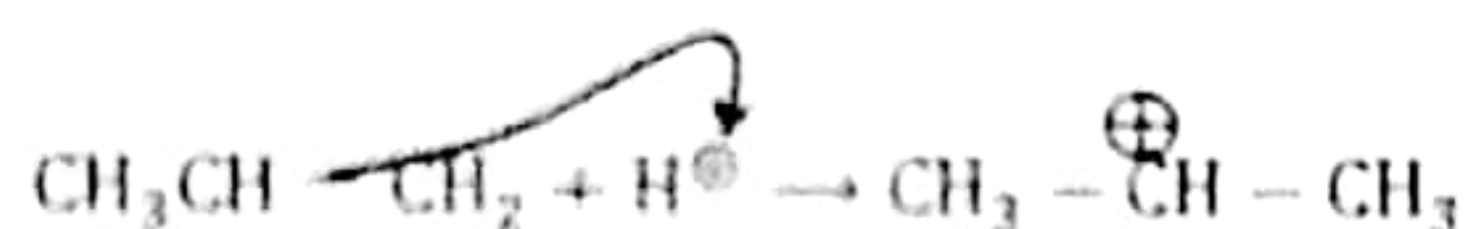
Cumene formation

Benzene reacts with propene under presence of acidic medium to give isopropylbenzene (cumene).

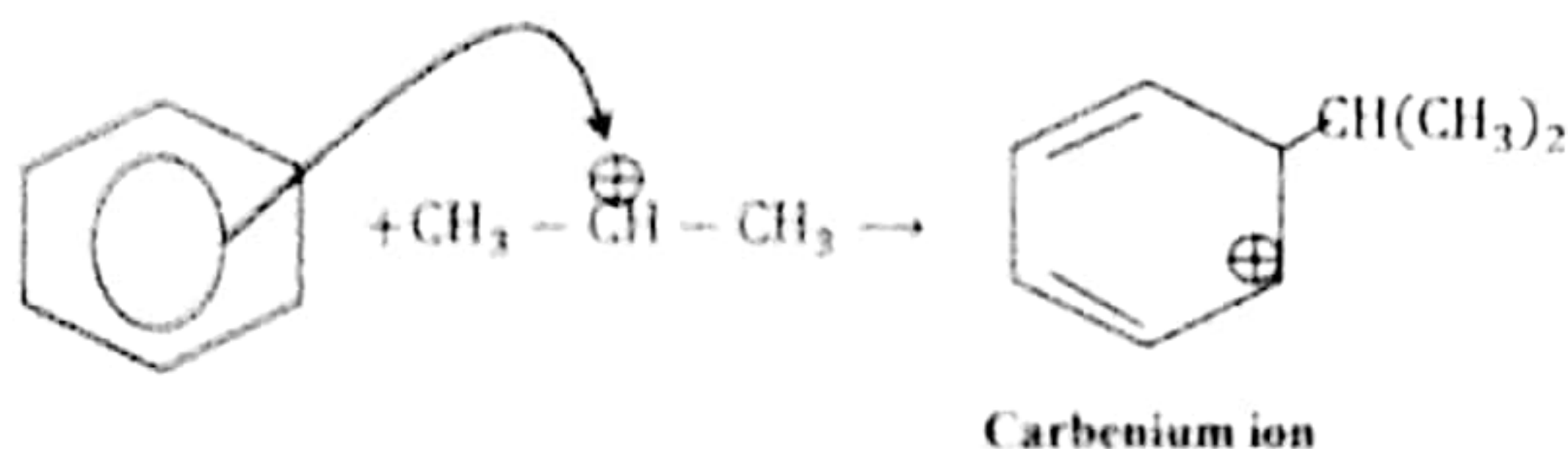


Mechanism:

1. Formation of an electrophile



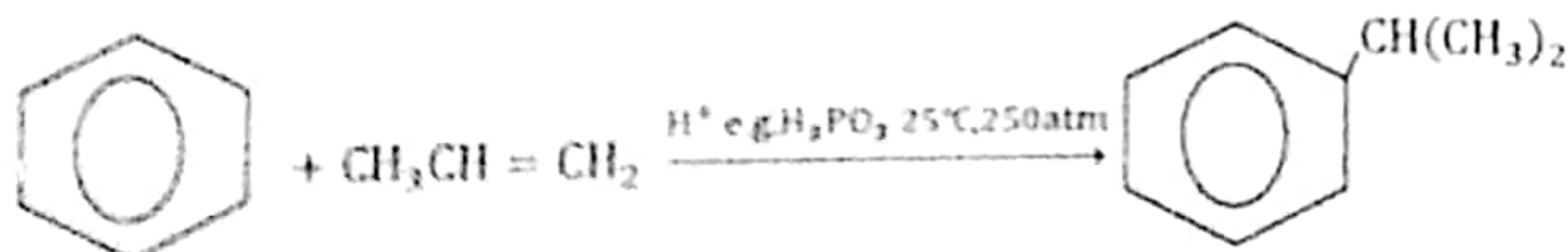
2. Formation of intermediate carbenium ion



3. Formation of product and regeneration of catalyst

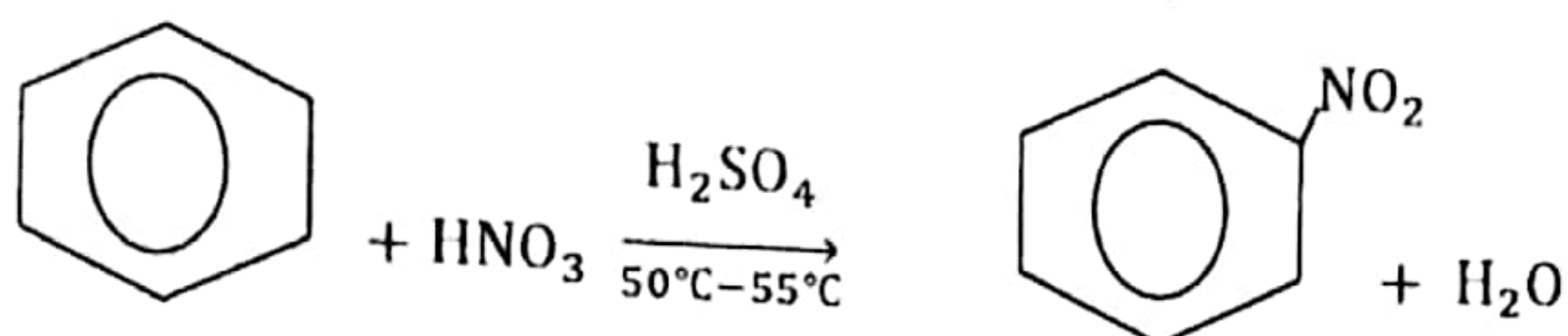


Hence the overall reaction is,



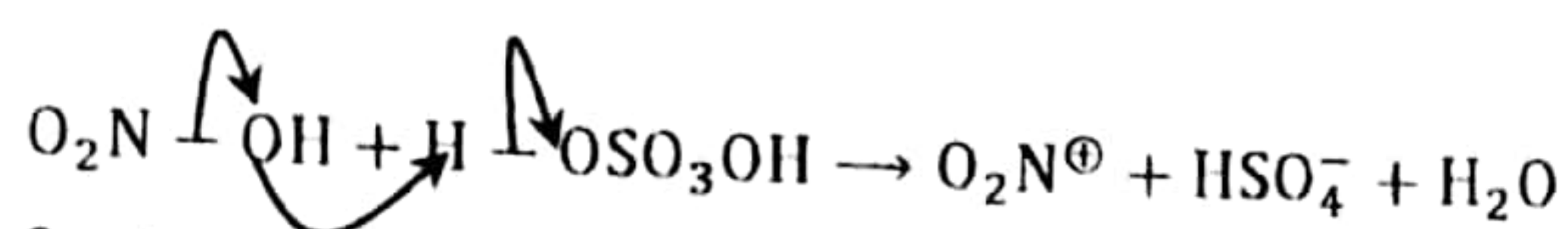
Nitration

Benzene reacts with concentrated nitric acid under presence of concentrated sulphuric acid at temperature range of $50^{\circ}\text{C} - 55^{\circ}\text{C}$ yielding nitrobenzene.

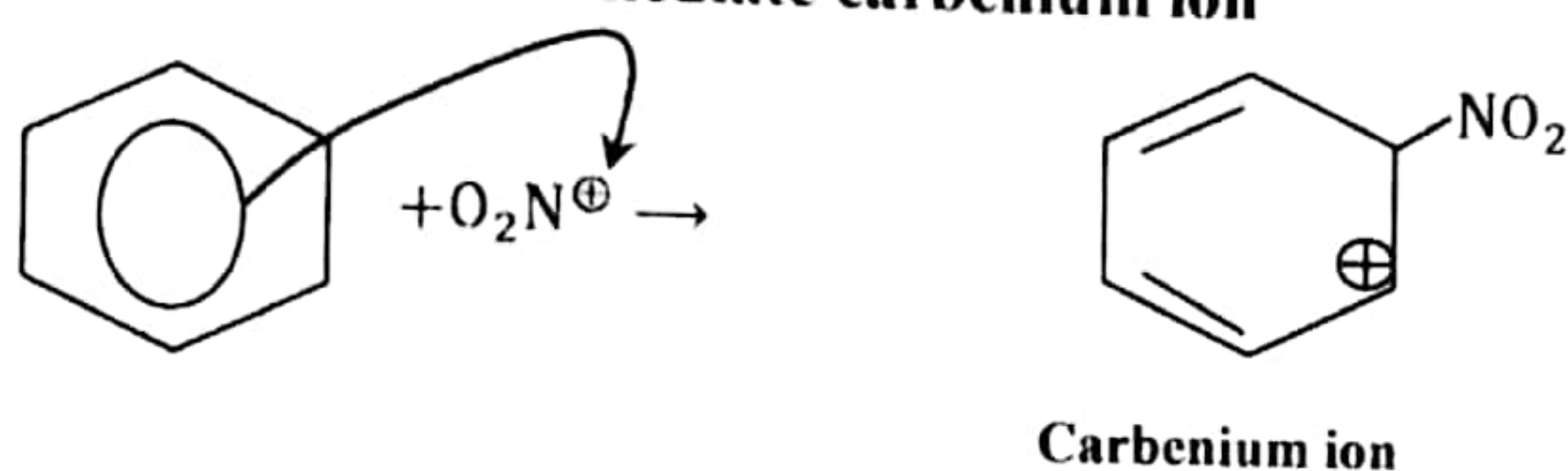


Mechanism:

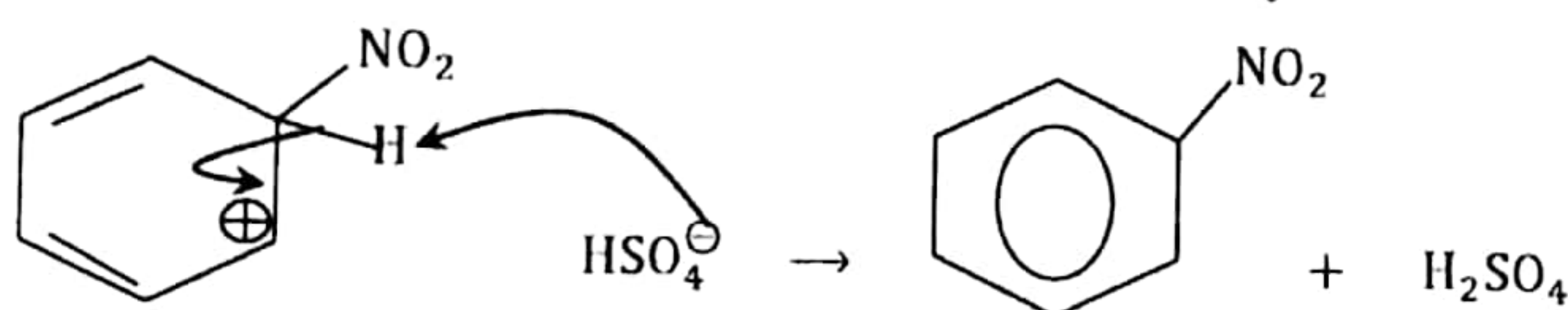
1. Formation of an electrophile



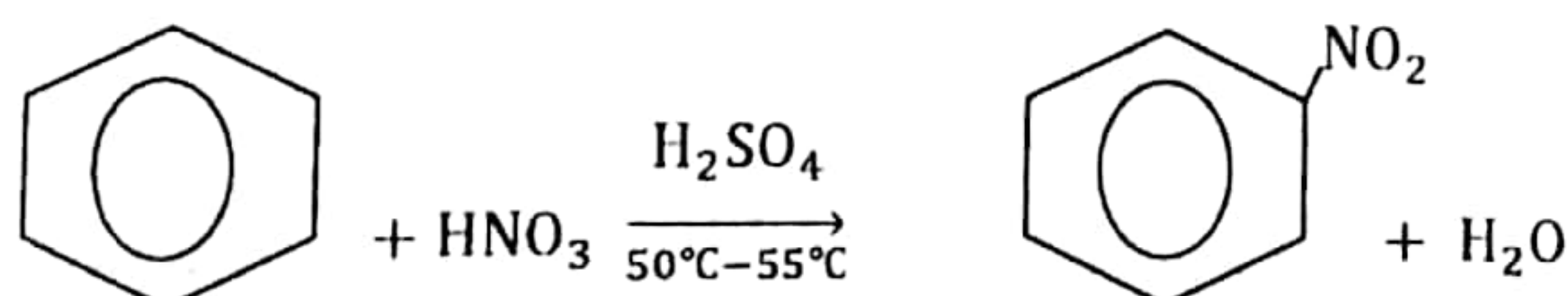
2. Formation of intermediate carbenium ion



3. Formation of product and regeneration of catalyst

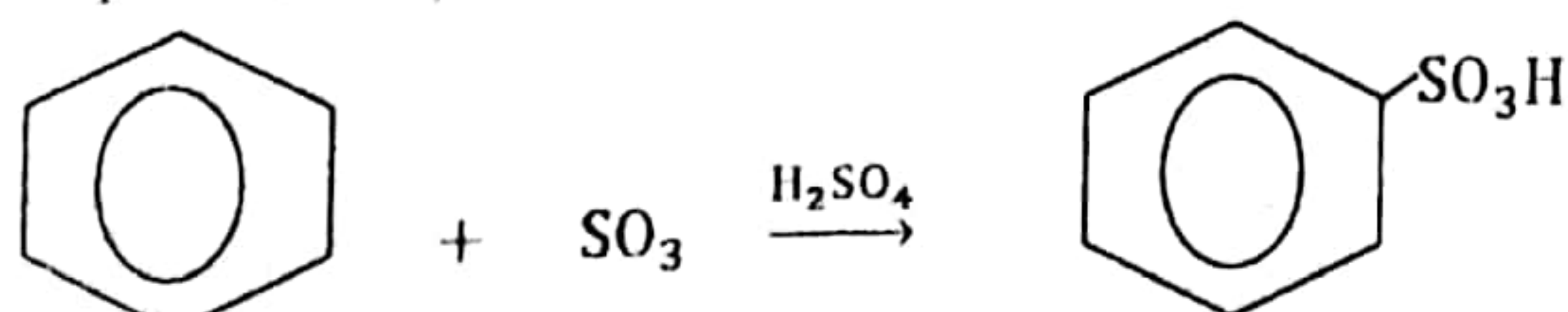


Hence the overall reaction equation is;



Sulphonation

Benzene reacts with sulphur trioxide (or concentrated sulphuric acid) to give sulphobenzene (Benzene sulphonic acid).

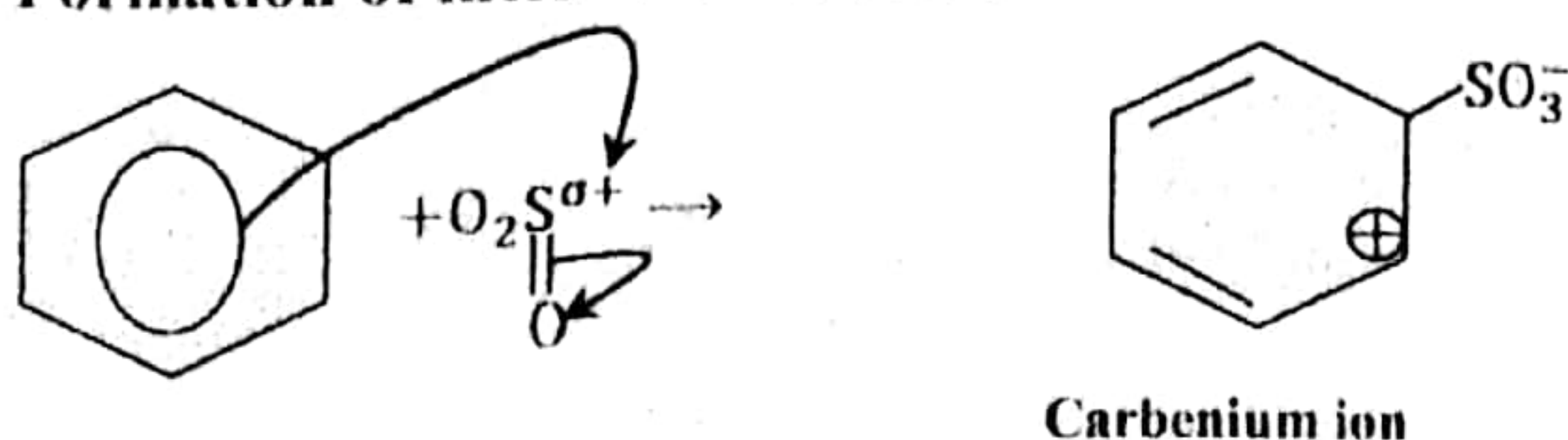


Mechanism:

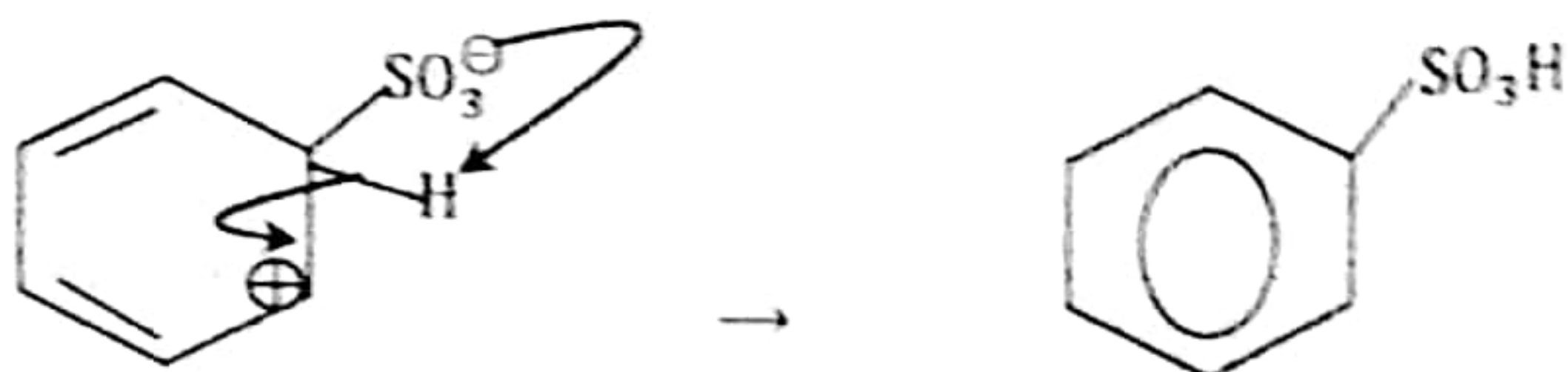
1. Formation of an electrophile

Sulphur trioxide itself is good electrophile.

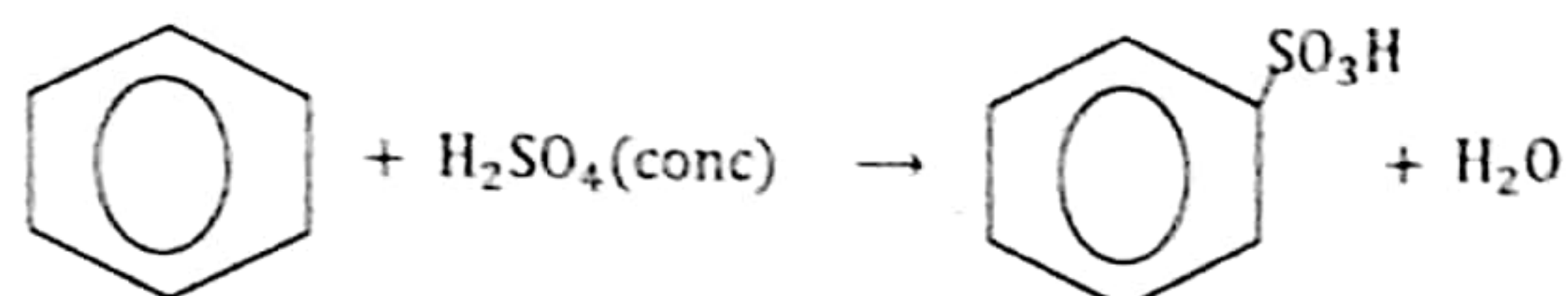
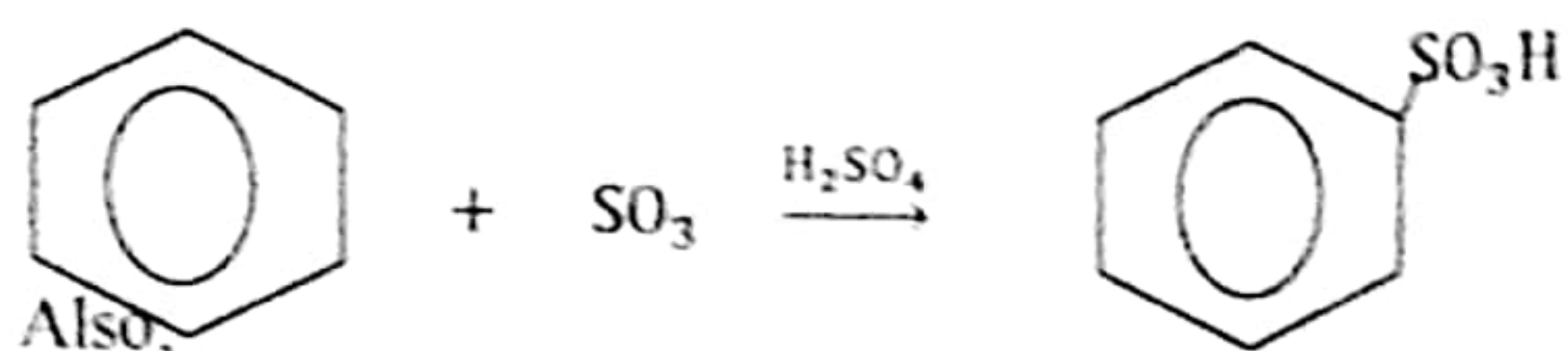
2. Formation of intermediate carbenium ion



3. Formation of product



Hence the overall reaction equation is;



In the above reaction sulphuric acid itself is good lewis acid (There is no need of another lewis acid catalyst).

More chemical reactions of benzene

Apart from electrophilic substitution reactions, benzene can undergo the following chemical reactions:

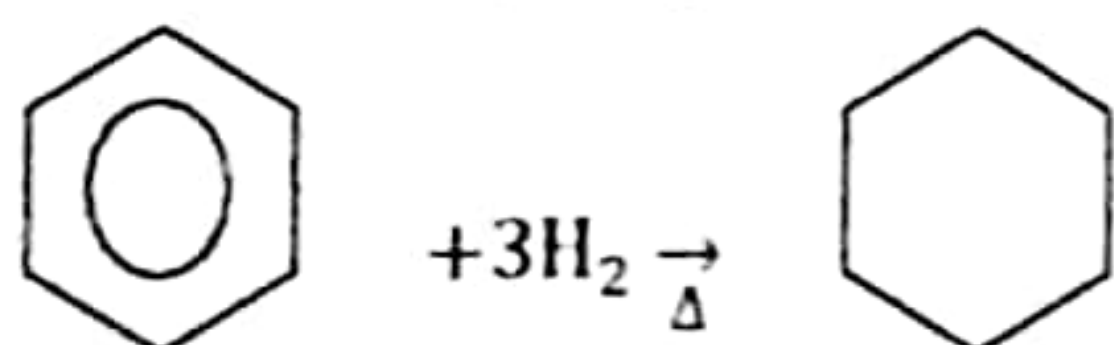
Addition reactions

Under vigorous condition benzene can undergo additions reactions. This includes:

- Hydrogenation and
- Halogenation

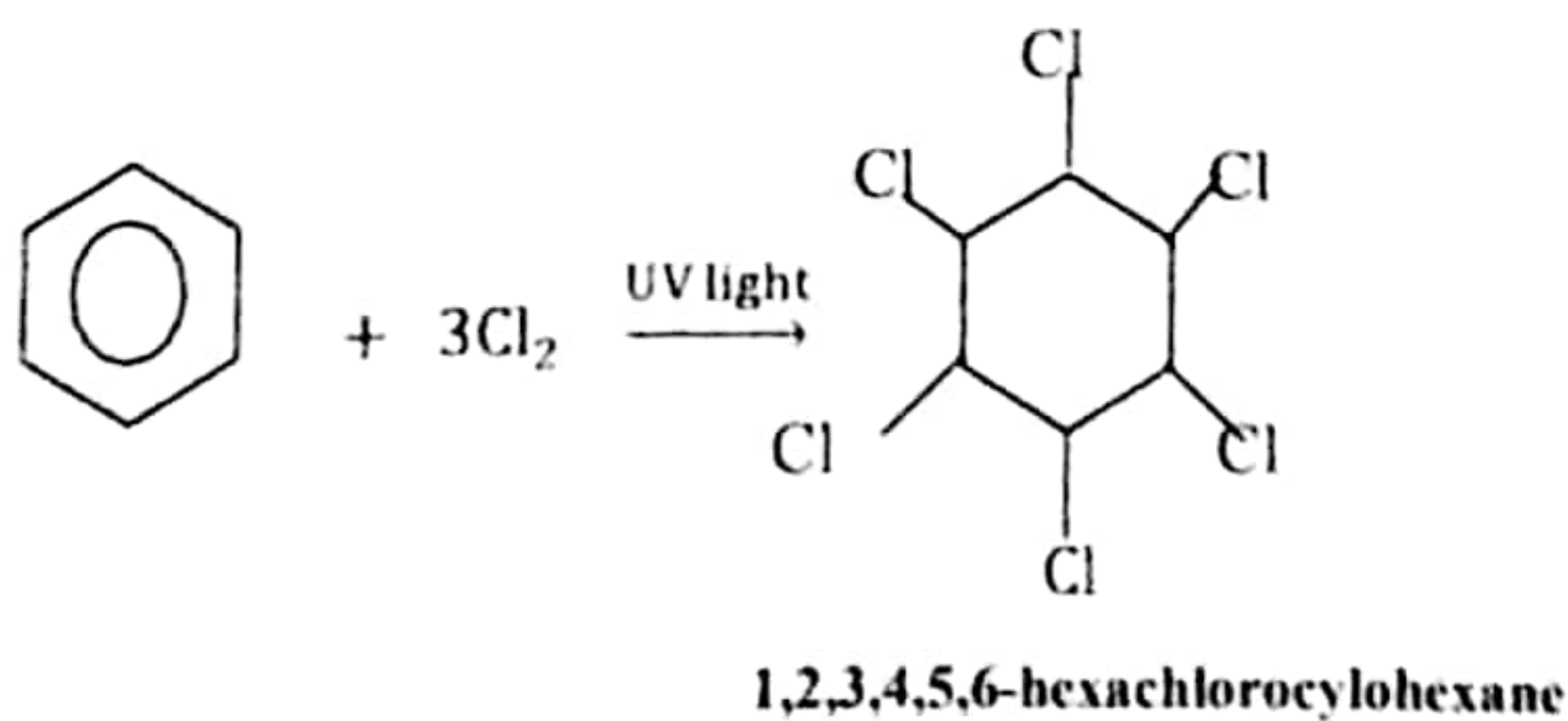
Hydrogenation

Benzene can react with hydrogen under presence of nickel or platinum catalyst yielding cyclohexane.



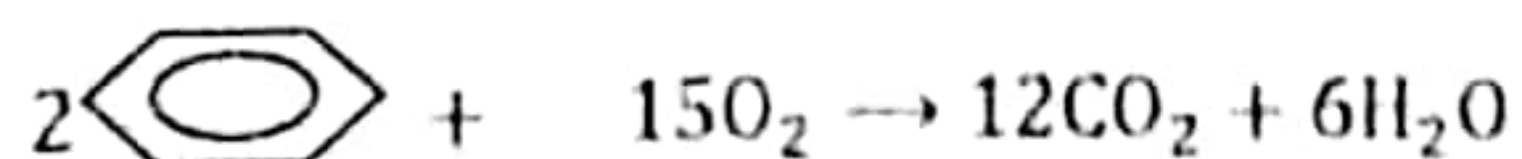
Chlorination

Under presence of u.v or very high temperature, benzene react with chlorine to give 1,2,3,4,5,6-hexachlorocyclohexane.



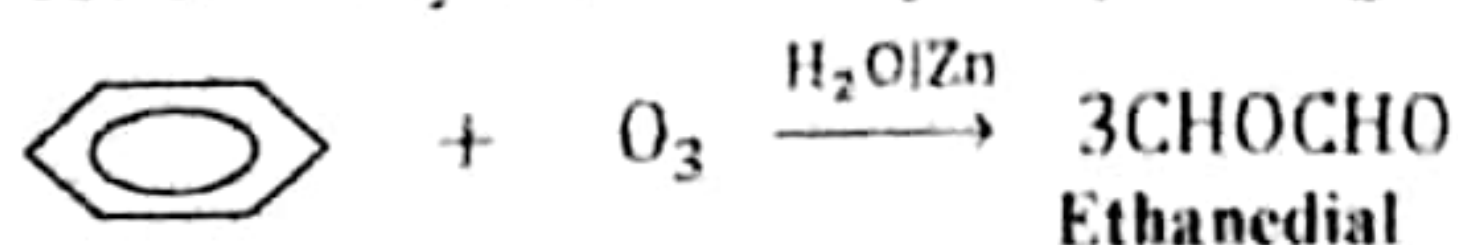
Combustion

Like other hydrocarbons benzene burn in oxygen, yielding carbondioxide gas and water on complete combustion.



Ozonolysis

Benzene reacts with ozone followed by reductive hydrolysis to give ethanedial.



PRACTICE EXERCISE 13

Problem 1

List down strength and weakness of:

- i. Kekule structure of benzene
- ii. Resonance structure of benzene

Problem 2

Outline manufacture of benzene from crude oil

Problem 3

Write chemical equation to show preparation of benzene from:

- i. Benzoic acid
- ii. Phenol
- iii. Sulphobenzene
- iv. Coke

Problem 4

Complete and balance the following organic reactions:

- i. $\text{C}_6\text{H}_6 + \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{HCl, AlCl}_3}$
- ii. $\text{C}_6\text{H}_6 + \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{H}_3\text{PO}_3}$
- iii. $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4(\text{conc}) \rightarrow$
- iv. $\text{C}_6\text{H}_6 + \text{O}_3 \xrightarrow{\text{H}_2\text{O, Zn}}$
- v. $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV}}$

Problem 5

Electrophilic substitution reaction is the common reaction in benzene. It always takes place under presence of Lewis acid catalyst.

- (i) What is the meaning of *electrophilic substitution reaction*? Give an example for the reaction.
- (ii) What are reasons for benzene to undergo electrophilic substitution reaction?
- (iii) Why Lewis acid catalyst is important is for benzene to undergo electrophilic substitution reaction although benzene is already nucleophilic.
- (iv) Give equations of at least other two reactions of benzene which are not electrophilic substitution reaction.

Chapter 14

ACTIVATORS AND DEACTIVATORS IN BENZENE

Reactivity of benzene towards electrophile (in electrophilic substitution reaction) depends on the electron density in benzene ring.

- If the electron density is high then benzene will be more reactive towards an electrophile and if it is low, then the benzene will be less reactive towards the electrophile.

So any factor, which affects the electron density in benzene ring is said to affect reactivity of benzene towards an electrophile.

- When a substituent in benzene increase electron density in benzene ring, then the substituent is said to increase reactivity of benzene towards an electrophile. In other words it is said to activate electrophilic substitution reaction of benzene and hence the substituent is known as **activator**.
- On another hand if the substituent decrease electron density in benzene ring then the substituent is said to decrease reactivity of benzene towards an electrophile, that is it said to deactivate electrophilic substitution reaction of benzene and hence the substituent is known as **deactivator**.

How can we recognise whether a substituent is activator or deactivator?

Before studying recognition of activators and deactivators; it is better to study first effect which cause activation and deactivation in benzene.

- There are two effects which cause activation in benzene.

- Positive inductive effect (+I)
- Positive mesomeric effect (+M)

Positive inductive effect (+I)

This is the effect which arises in the organic compounds as a result of partial movement of an electron pair towards the functional group (in this case benzene ring).

- Thus positive inductive effect brings activation to benzene by partial supply of electrons towards the benzene ring. It caused by **alkyl groups**.

Positive mesomeric effect (+M)

This is the effect which arises in the organic compound as a result of total movement of an electron pair towards the functional group (in this case benzene ring) and then moving back again to its original position within the same molecule.

- Thus +M brings activation to benzene by total supply of an electron pair towards the benzene ring.

Substituents which cause +M (in benzene) is the one with atoms possessing lone pair or negatively charged atom and itself directly bonded to another atom by sigma (δ) bond. Examples are **OH**, **NH₂**, **RO** and **X** where **X** is halogen.

- On another hand there are two effect which cause deactivation in benzene;

- Negative inductive effect (−I)
- Negative mesomeric effect (−M)

Negative inductive effect (–I)

This is the effect which arises in organic compound as result of partial withdraw of an electron pair from functional group ((in this case benzene ring).

- So negative inductive effect do deactivation in benzene by partial withdraw of electron pair from benzene ring.

Substituents which cause –I are strong electronegative atom or electron attracting radicals. Examples are **OH, NH₂, RO** and **X**.

Negative mesomeric effect (–M)

This is the effect which arises in organic compounds as result of total withdraw of an electron pair from functional group (in this case benzene ring) and then moving back again to its original position within the same molecule.

- So –M brings deactivation to benzene by total withdraw of an electron pair from benzene ring.

Substituent which cause –M is the one with atoms possessing lone pair or negatively charged electron and itself is bonded to another atom by π -bond. Examples are: **COOH, CONH₂, COOR, CN, SO₃H** and **NO₂**

Contradiction!

From the above discussion, it can be recognised that the same substituents (**OH, NH₂, RO** and **X**) cause both activation by +M and deactivation by –I!

- Don't worry! Here is the rule to overcome such contradiction.

In most cases where there is a competition between inductive effect and mesomeric effect; is the mesomeric effect which outweighs the inductive effect.

- This is because, while inductive effect involves partial movement of electron pair, mesomeric effect involves total movement of electron pair.

Thus when the same specie cause –I and +M effect, the effect which will be considered is +M and the specie will be **activator**.

Exceptional of the rule

Halogens are exceptional of the above explanation. In halogens inductive effects tends to outweighs mesomeric effects, **why?**

Reason:

Halogens being very strong electronegative elements exert very strong negative inductive effect.

On another hand, halogens have maximum number of lone pair electrons (three lone pairs are available) thus making them less available in participation of mesomeric effect due to large repulsion existing between those lone pairs.

- So while halogens exert very strong negative inductive effect they also exert very weak mesomeric effect (–M) hence in halogens, inductive effect outweighs mesomeric effect.

In two sentences we can conclude that:

- All substituents which cause positive inductive effect and those which cause positive mesomeric effect with exception of halogens are **activators**.

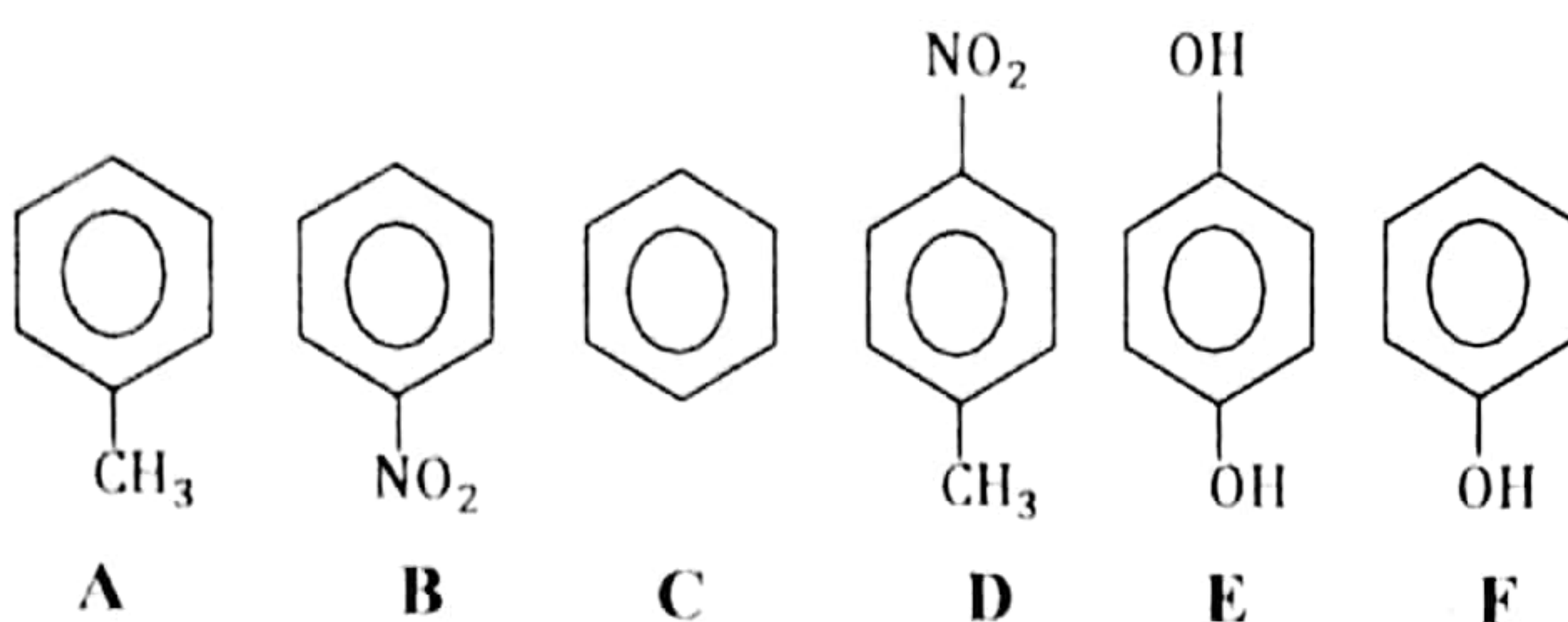
- All substituents which cause negative mesomeric effect with additional of halogens (which cause $-I$) are **deactivators**.

Very important to understand that, all positively charged substituents are strong deactivators regardless to their bonding structure whether is sigma (σ) or pi (π). For example $-\text{NH}_2$ but $\text{H}_3\text{N}^+ -$ is deactivator.

Example 1

Arrange the following compounds (labelled A to F) according to their reactivity towards:

- Electrophile
- Nucleophile



Solution

- $$\text{E} > \text{F} > \text{A} > \text{C} > \text{D} > \text{B}$$

↓
decrease in reactivity towards E^+
- $$\text{B} > \text{D} > \text{C} > \text{A} > \text{F} > \text{E}$$

↓
decrease in reactivity towards Nu^-

Example 2

Explain why alkylation of nitrobenzene is much slower than that of methylbenzene.

Solution

Alkylation in given compounds are electrophilic substitution reaction. Presence of nitro group which is an electron withdrawing group (deactivator) in nitrobenzene deactivates its reaction toward electrophile while presence of methyl group which is electron releasing group (activator) in methylbenzene activates its reaction towards electrophile and hence alkylation of nitrobenzene become slower than that of methyl benzene.

PRACTICE EXERCISE 14

Problem 1

Classify the following substituents as activators and deactivators

- | | |
|--|--|
| i. $-\text{CN}$ | iii. $\text{CH}_2 = \text{CH} -$ |
| ii. $-\text{OH}$ | iv. $\text{CH}_2 = \text{CH} - \text{CH}_2 -$ |
| v. $-\text{CH} = \text{CH} - \text{CH}_3$ | vi. $-\text{NH}_3$ |
| vii. $-\text{Cl}$ | viii.  |
| ix. $-\text{NH} - \text{CO} - \text{CH}_3$ | x. $-\text{SO}_3\text{H}$ |
| xi. $-\text{NO}_2$ | xii. $-\text{COCl}$ |
| xiii. $-\text{COOH}$ | xiv. CH_2CH_3 |
| xv. $\text{CH}_3\text{O} -$ | xvi. $\text{H}_2\text{N} -$ |

Problem 2

Sulphonation of cumene is relatively faster than that of benzene. Explain.

Problem 3

Between anisole and toluene, which one is more reactive towards bromoethane? Give reasons for your choice.

Problem 4

Between aniline and chlorobenzene which one undergoes acylation reaction at lower temperature? Give reasons for your choice.

Chapter 15

DIRECTING EFFECT IN SUBSTITUTED BENZENE

INTRODUCTION

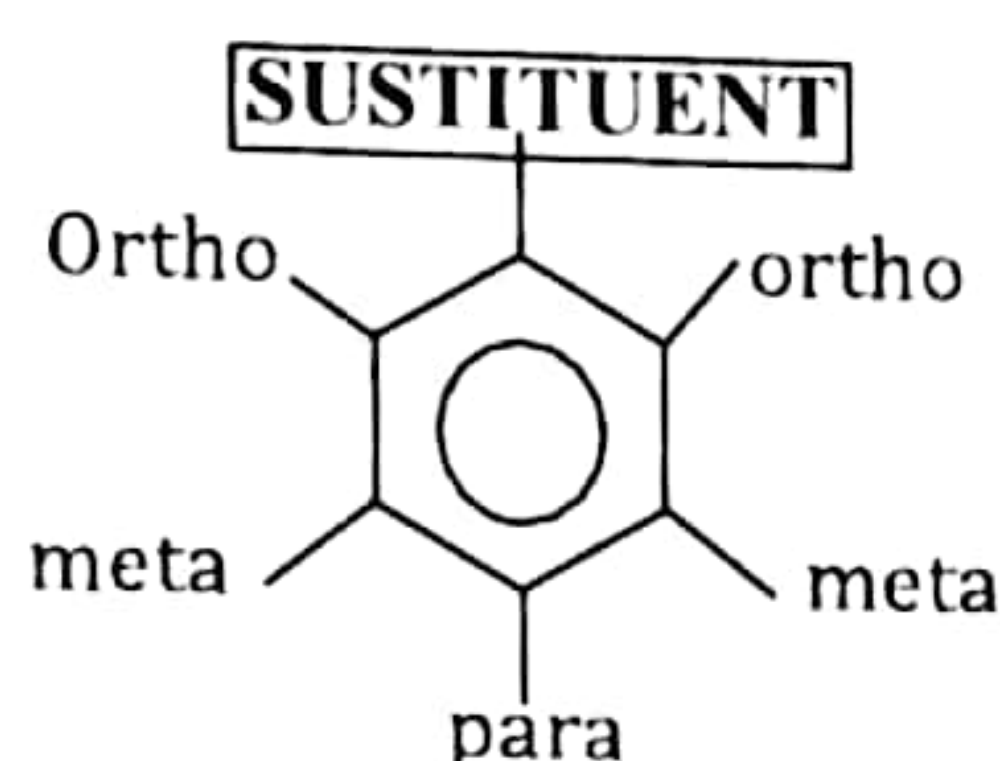
Substituted benzene tends to undergo electrophilic substitution reactions in similar way to benzene.

- However there are two things that are going to be affected by presence of the substituent with respect to electrophilic substitution reaction in the benzene ring.

1. Substituent in benzene affects reactivity of benzene towards electrophile. This has been discussed in the **chapter 14**.

2. Substituent in benzene directs (influences) position at which incoming electrophile will attach. This is what we are going to discuss in this chapter.

Carbons in benzene with only one substituent group can be termed as follows;



That is:

- **ortho** is **1,2-position** and it is denoted by small letter '**o**'
- **meta** is **1,3-position** and it is denoted by small letter '**m**'
- **para** is **1,4-position** and it is denoted by small letter '**p**'

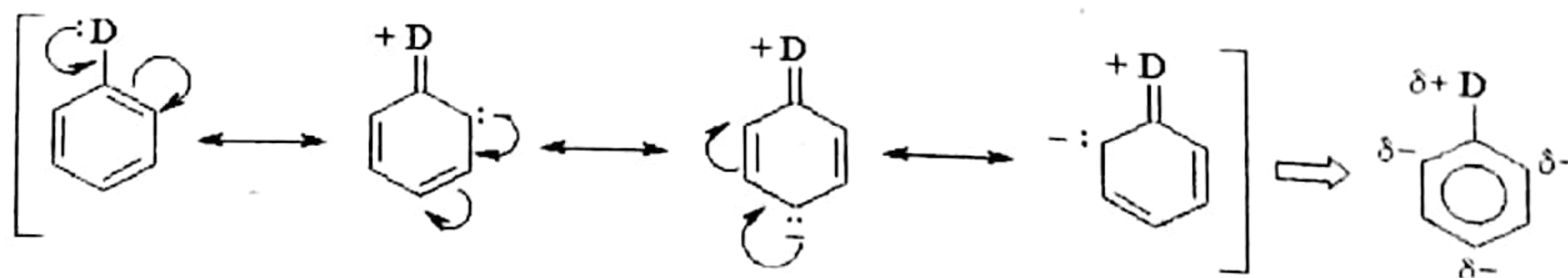
DIRECTING EFFECT OF ACTIVATORS

If the substituent is activator, then it tends to direct an incoming electrophile at ortho and para positions, that is all activators are ortho-para directors. This can be explained by considering:

- Position of carbanion and
- Stability of intermediate carbenium ion

1. Position of carbanion

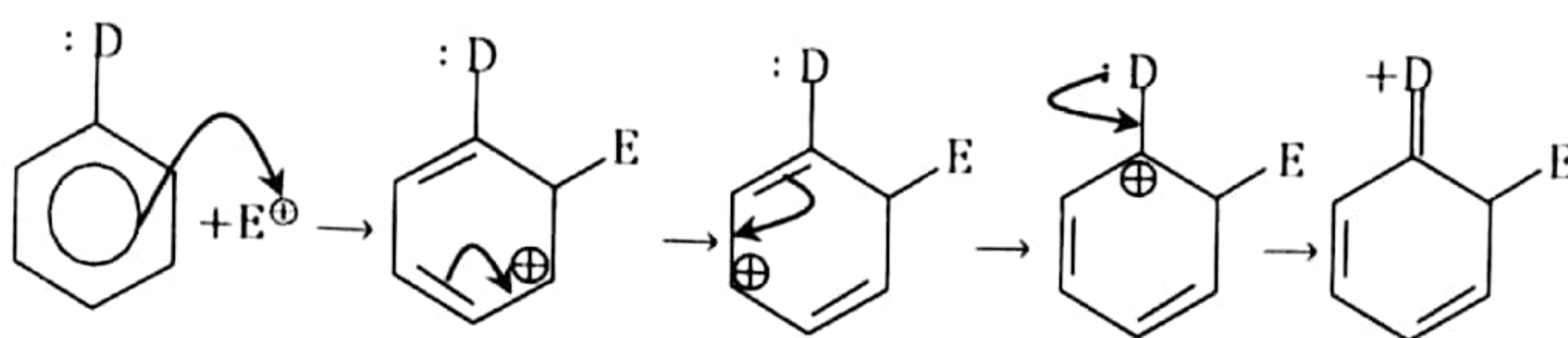
If '**D**' represents any activator which donates electron to benzene ring by positive mesomerism; then the mesomerism can be shown as follows:



From the above mesomerism (+M); it can be seen that despite the fact that D (activator) increase electron density throughout the benzene, ortho and para positions are more affected and hence ortho and para carbons become better site for incoming electrophile.

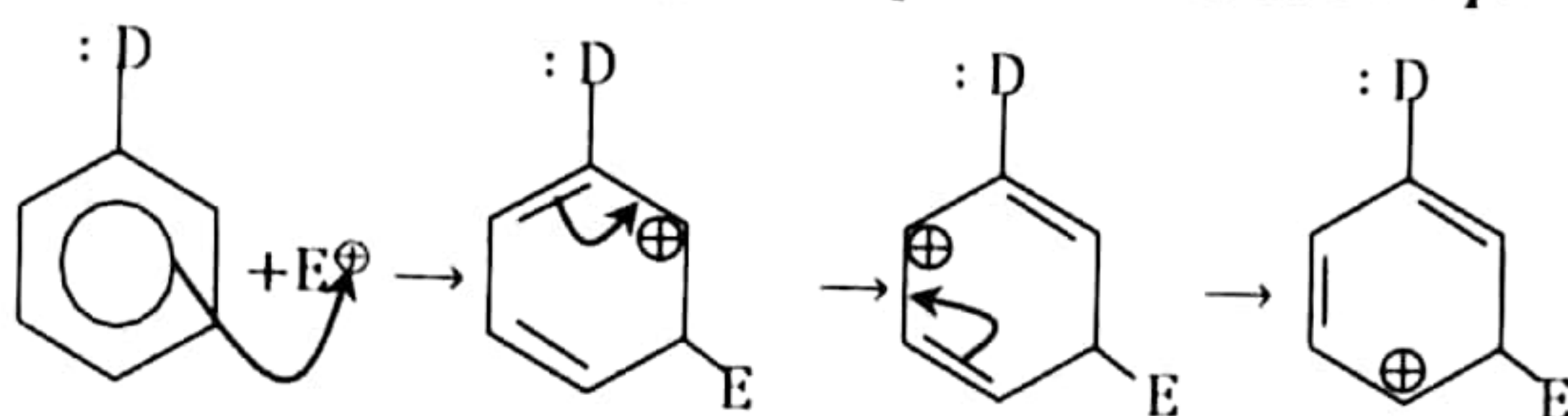
2. Stability of intermediate carbenium ion

1st case: *If an incoming electrophile attaches at ortho position*



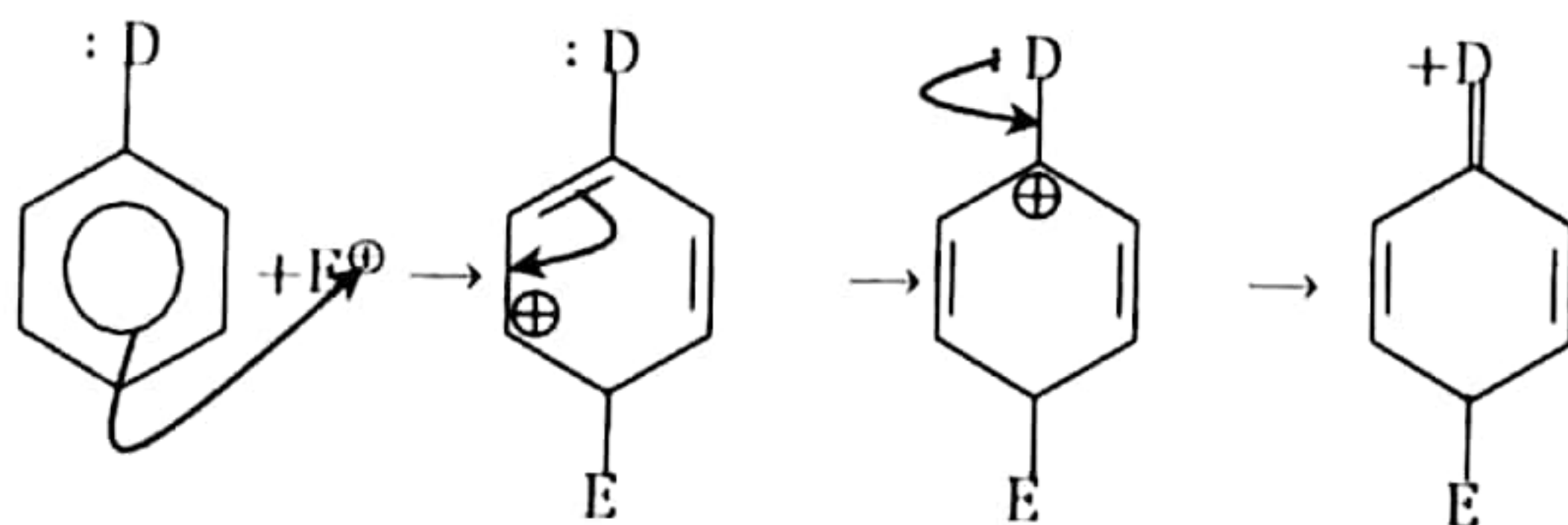
In the above mesomerism it is clearly understood that intermediate carbenium ion is stabilised by lone pair electrons in the electron donating group and hence it is more stable.

2nd case: *If an incoming electrophile attaches at meta position*



In this case intermediate carbenium ion is not stabilised by lone pair electrons of the electron donating group and hence it is less stable.

3rd case: *If an incoming electrophile attaches at para position*



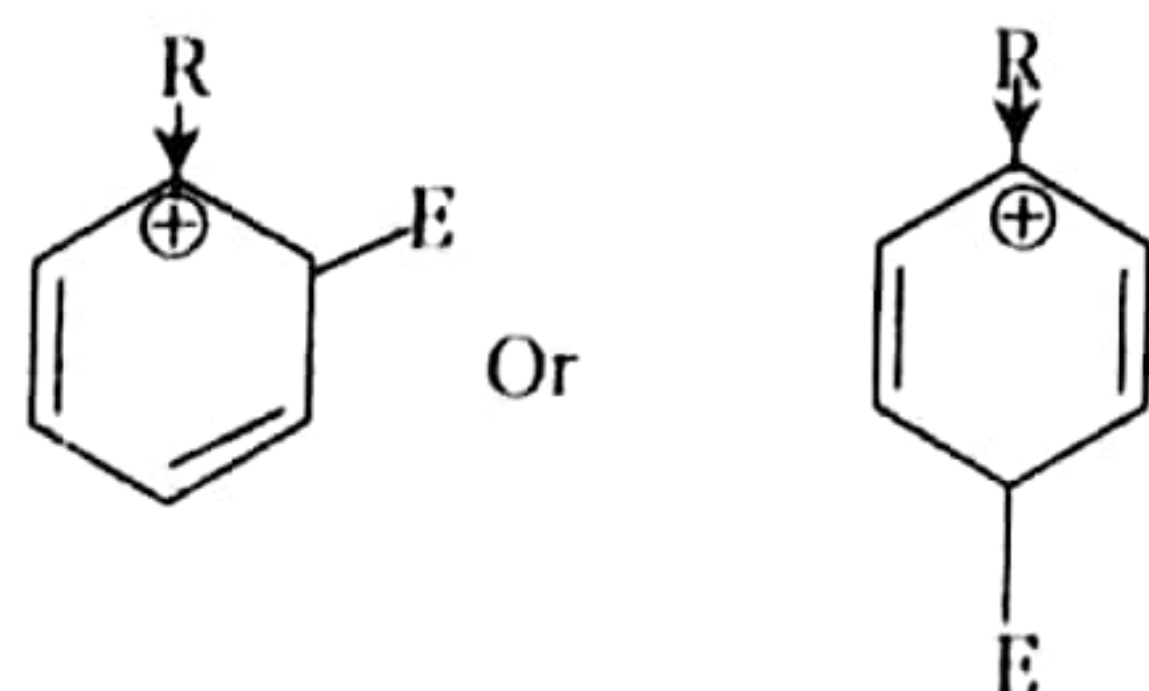
In this case carbenium ion is stabilised by lone pair of the electron donating group hence it is more stable.

Conclusion:

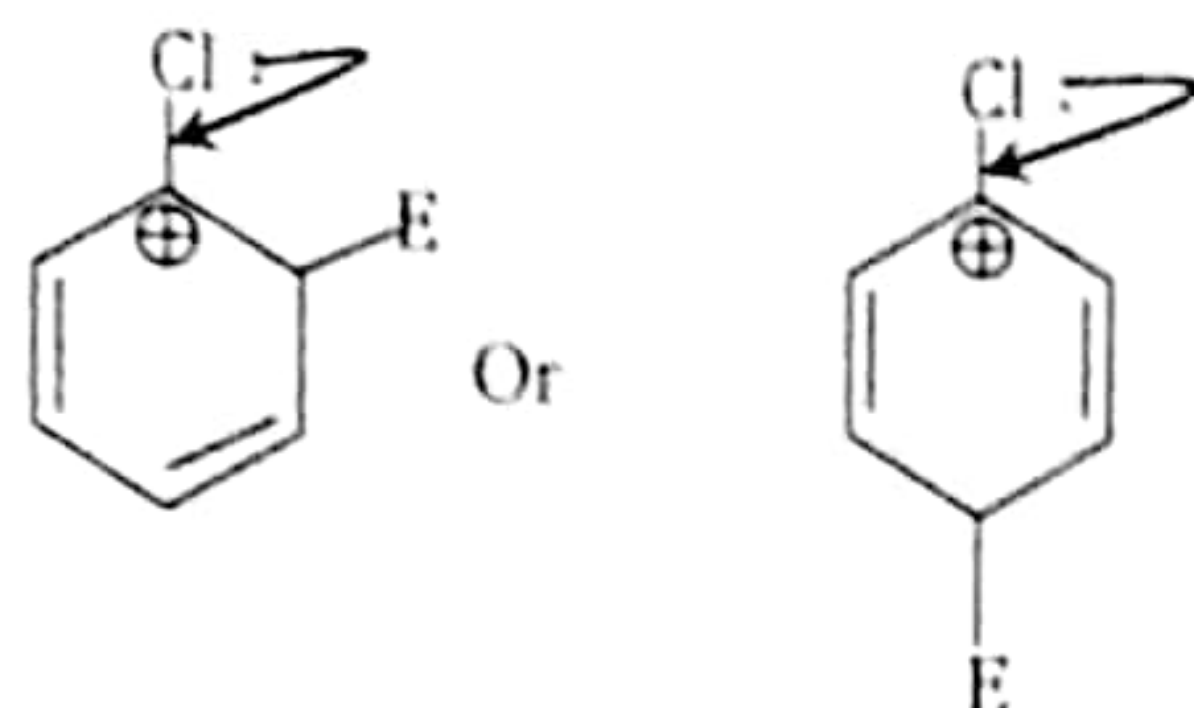
Since carbenium ions formed in 1st and 3rd case are more stable than that formed in 2nd case, ortho and para positions are more preferred sites for an incoming electrophile.

The reader should understand that:

- Alkyl group does not cause positive mesomeric effect in benzene ring. So its ortho-para directing effect cannot be explained by position of carbanion.
- Its directing effect is explained by only one factor of stability of intermediate carbenium ion.
- It acts as ortho-para directors by doing partial neutralisation of positive charge formed on the adjacent carbon (The partial neutralisation is done by positive inductive effect exerted by alkyl groups) thus stabilising the intermediate carbenium ion.



- Although halogens are deactivators, but like activators halogens are ortho-para directors due to stability intermediate carbenium ion. This is simply because despite the fact that lone pairs in halogens have not good participation in mesomerism for reason which has explained, but in presence of positive charge on adjacent carbon lone pair electrons participate in neutralizing positive charge on the carbon.



Among the two products (ortho product and para product) in most cases para product is major product, why?

Reason:

Due to steric hindrance exerted by the substituent originally present in benzene, and carbons which are closer to the substituent experience the effect strongly. Thus an incoming electrophile is more favoured to substitute at para carbon which is far from the substituent.

But if the substituent is small, the ortho product becomes major product, why?

Reason:

Small sized substituents have very small steric hindrance so making an incoming electrophile to substitute just at ortho carbons (for every two ortho carbons there is only one para carbon)

- Generally the smaller the substituent the greater probability of forming ortho product.

DIRECTING EFFECT OF DEACTIVATORS

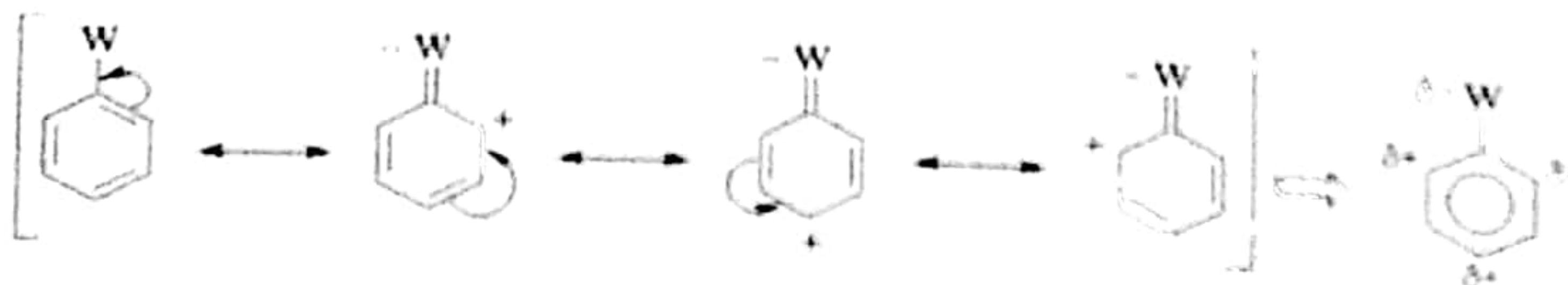
All deactivators with exception of halogens directs an incoming electrophile at meta position, that is deactivators (with exception of halogens) are meta directors.

- This can be explained by considering:

- Position of carbocation and
- Stability of intermediate carbenium ion

1. Position of carbocation

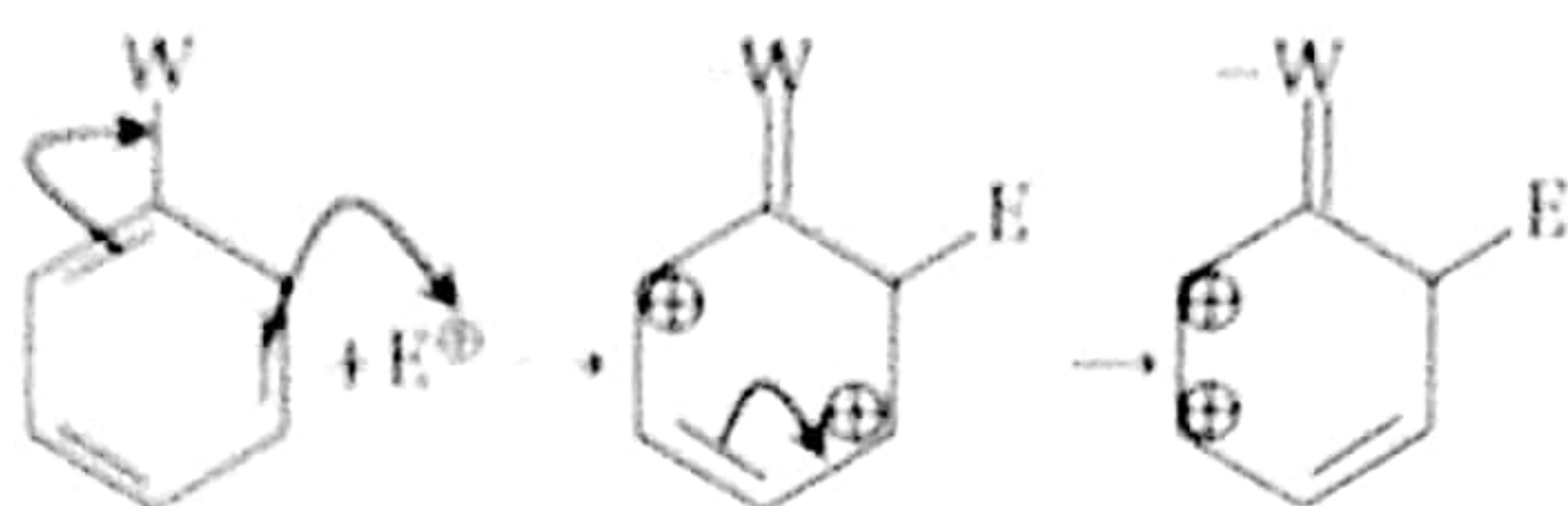
If 'W' represents an electron withdrawing group in benzene; then the negative mesomerism in the benzene ring can be shown as follows:



From the above shown mesomerism it can be seen that, despite the fact that the electron withdrawing group deactivates the whole benzene ring, ortho and para positions are more effected and hence meta carbon become better position for an incoming electrophile.

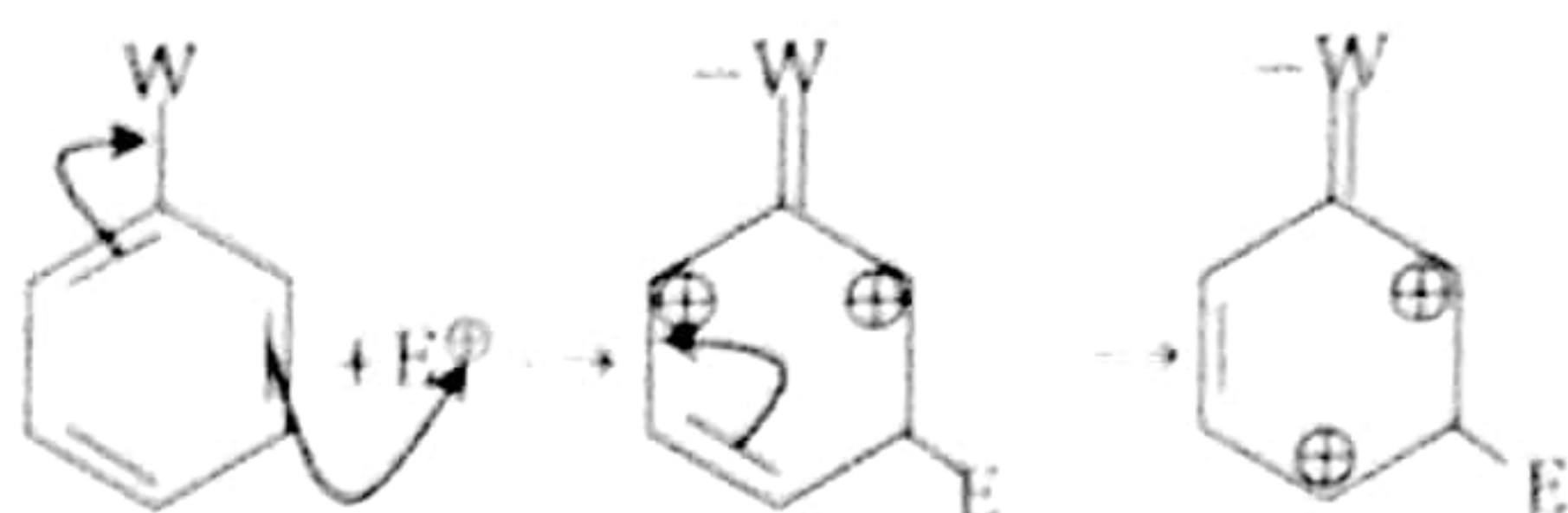
1. Stability of intermediate carbenium ion

1st case: *If an incoming electrophile attaches at ortho position.*



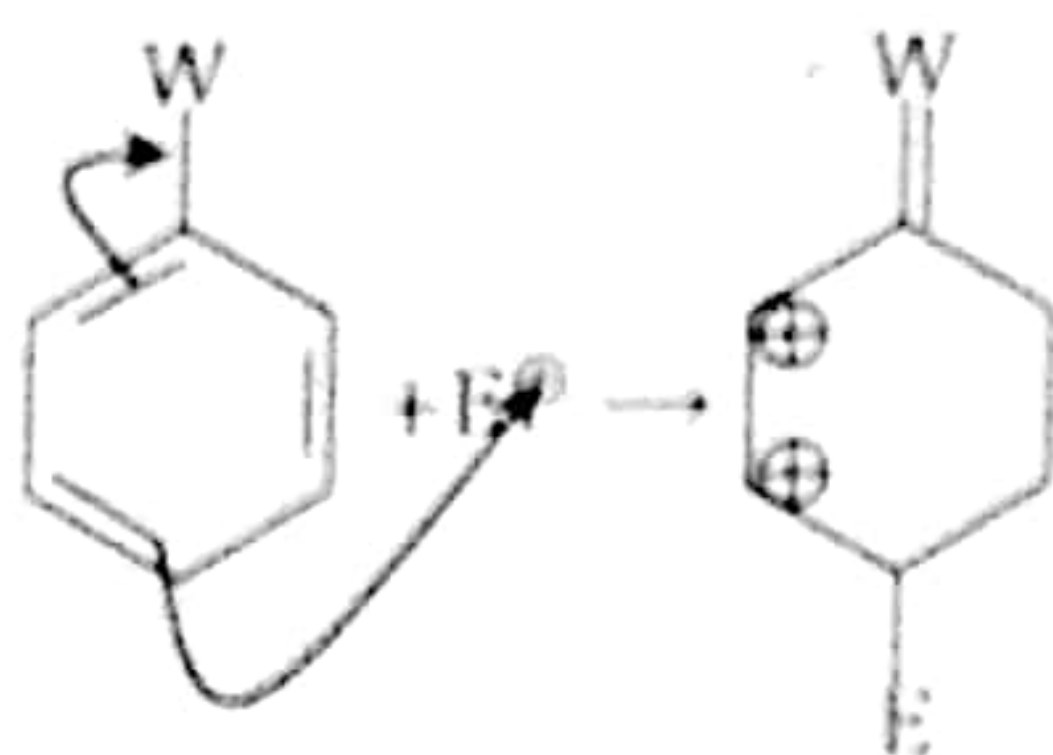
Intermediate carbonium is very unstable as result of very large repulsion force between closer positively charged ions in adjacent carbon atoms

2nd case: *If an incoming electrophile attaches at meta position*



Here the positively charged carbons are not adjacent. So the carbenium ion is slight stable.

3rd case: *If an incoming electrophile attaches at para position*



Intermediate carbenium ion formed in this case is very unstable as result of very large repulsion force between closer positively charged ions in adjacent carbons.

Conclusion:

Intermediate carbenium ion formed in 2nd case is more stable than in 1st and 3rd cases and hence meta position is better site for incoming electrophile.

Summary on directing effect

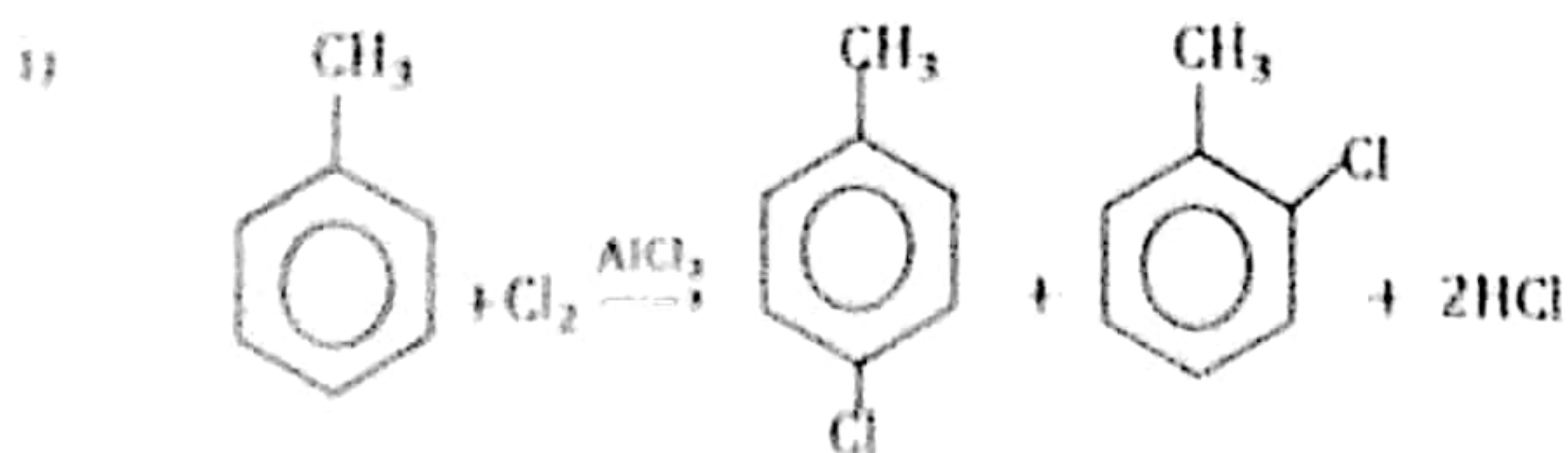
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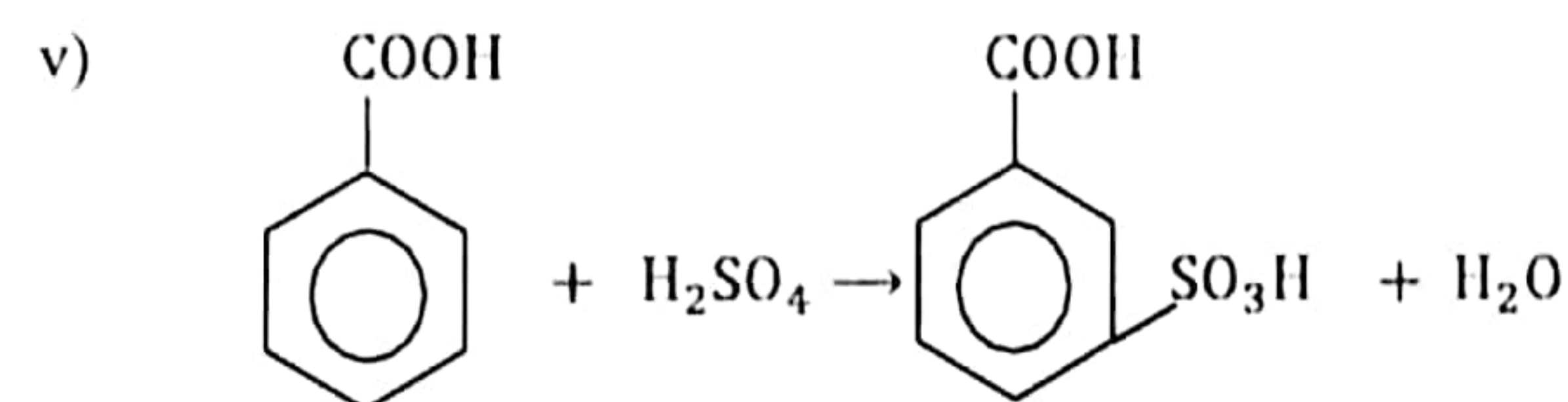
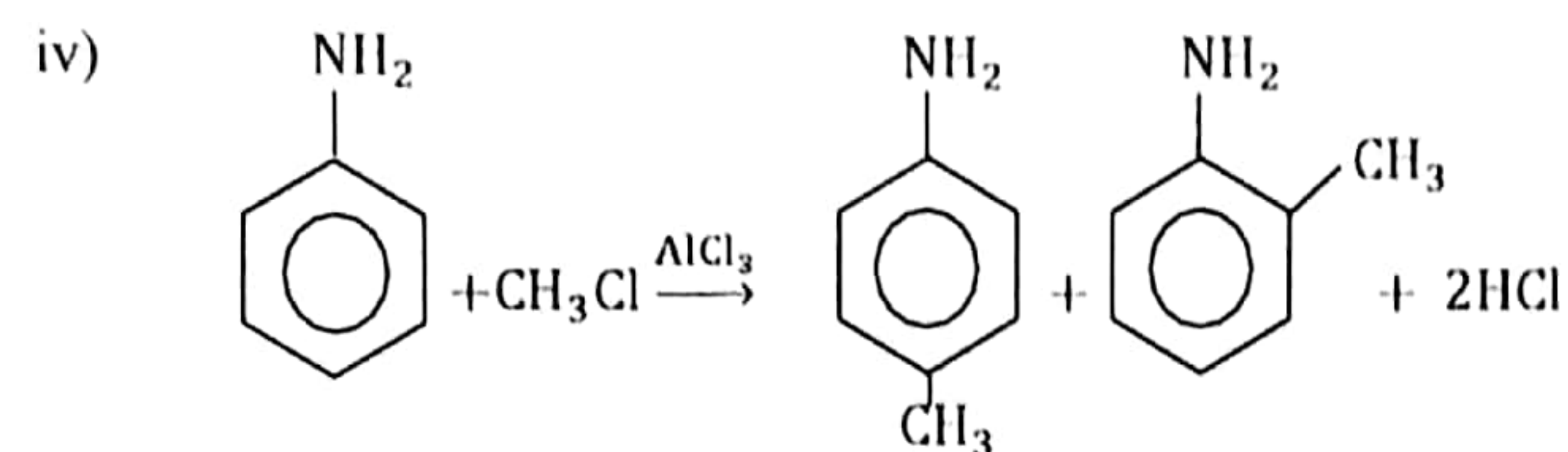
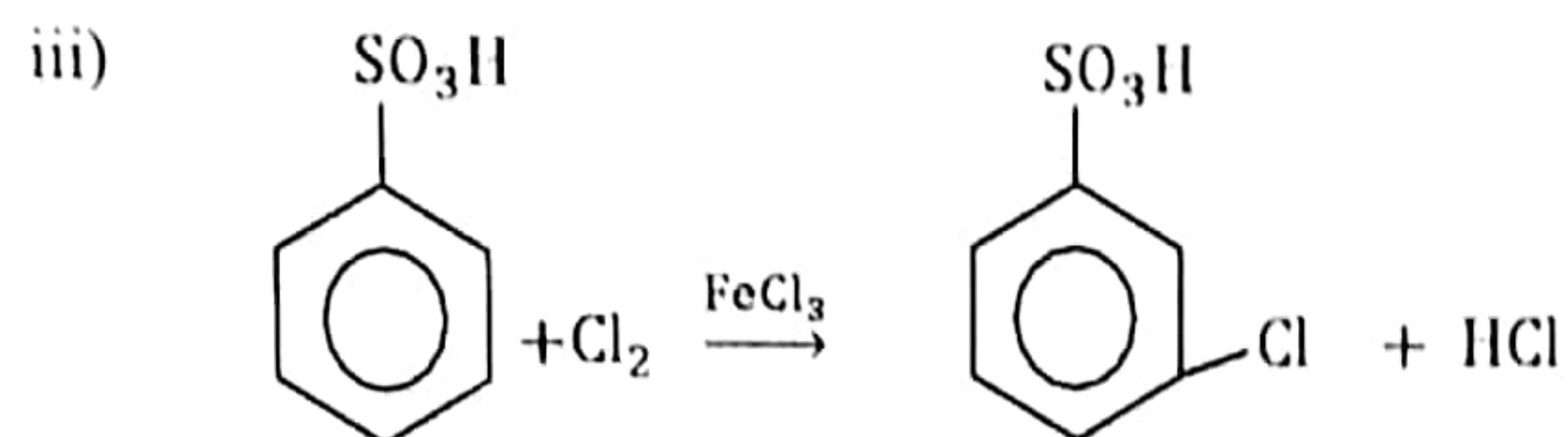
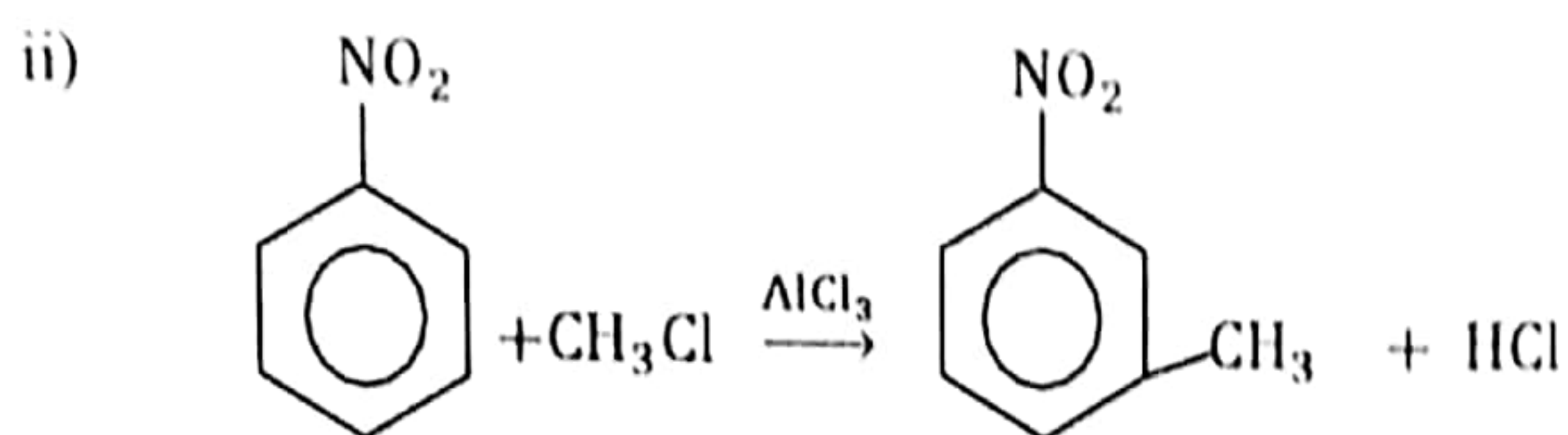
Where **EWG** and **EDG** stand for electron withdrawing group and electron donating group respectively. H is standard (reference) and has no effect.

Worked examples

Example 1

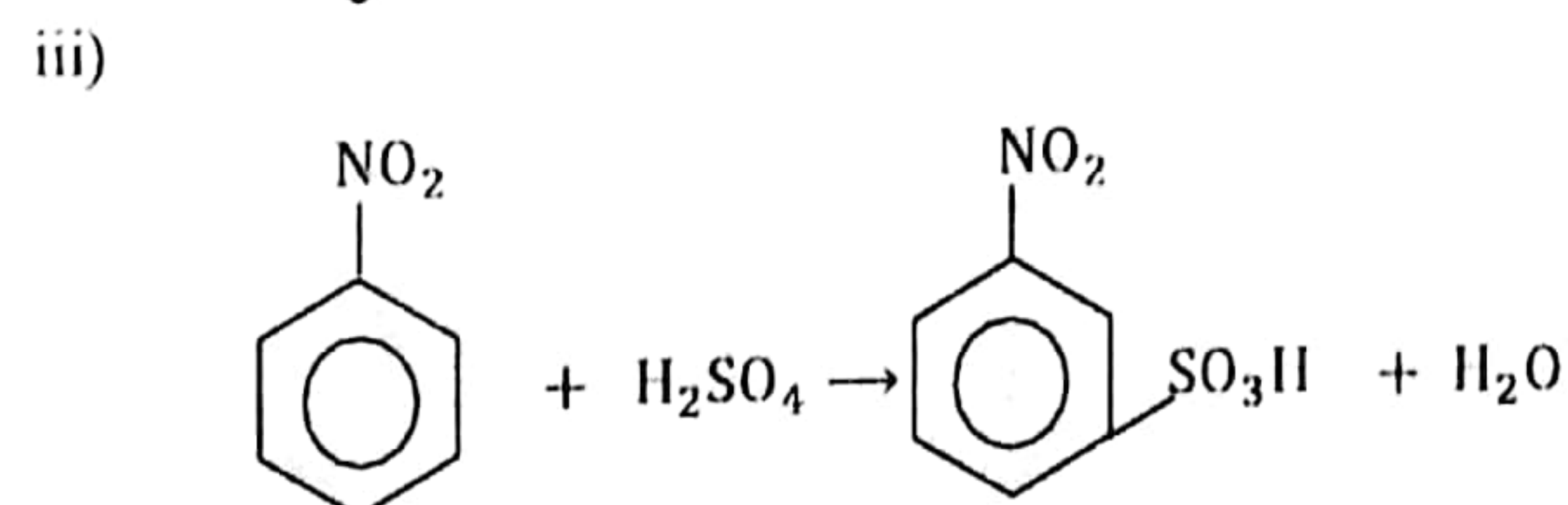
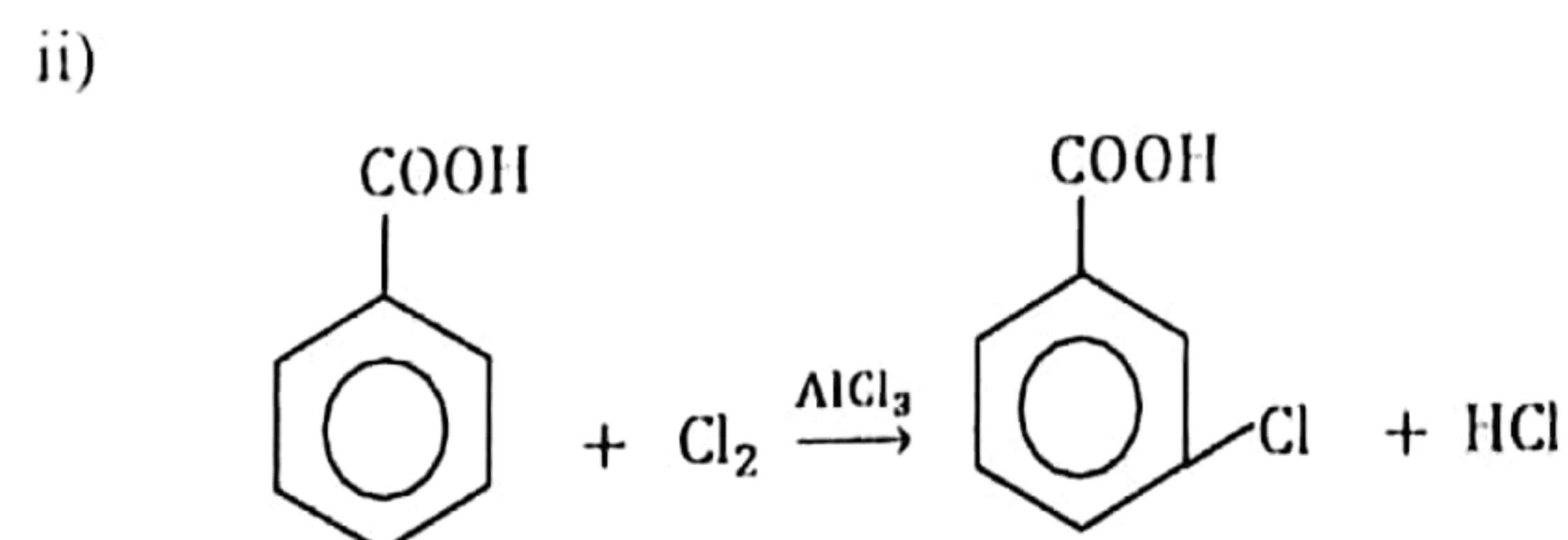
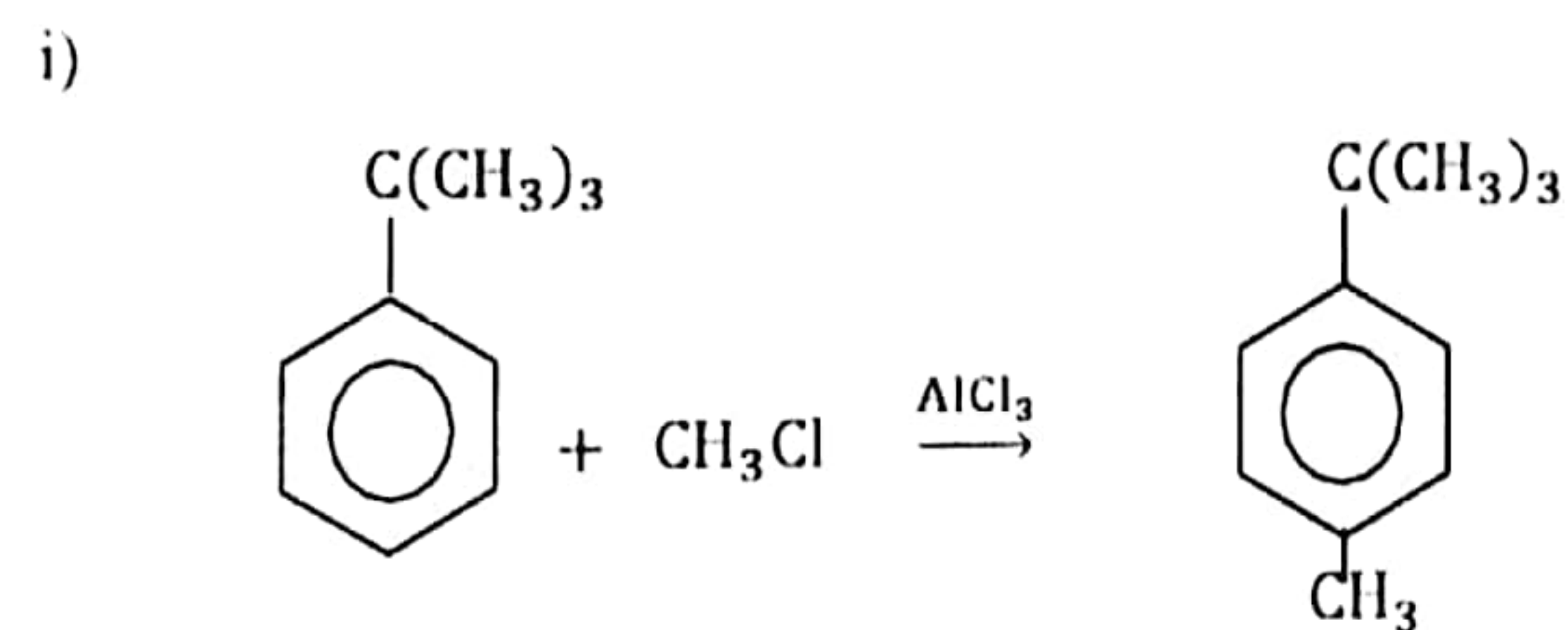
Complete the following organic reactions;

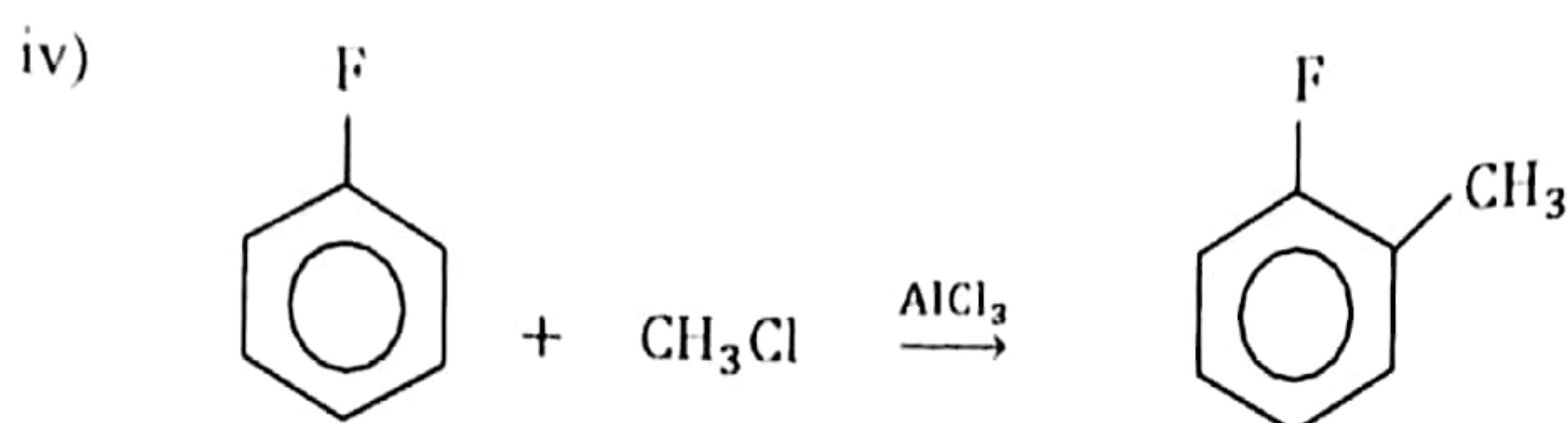




Example 2

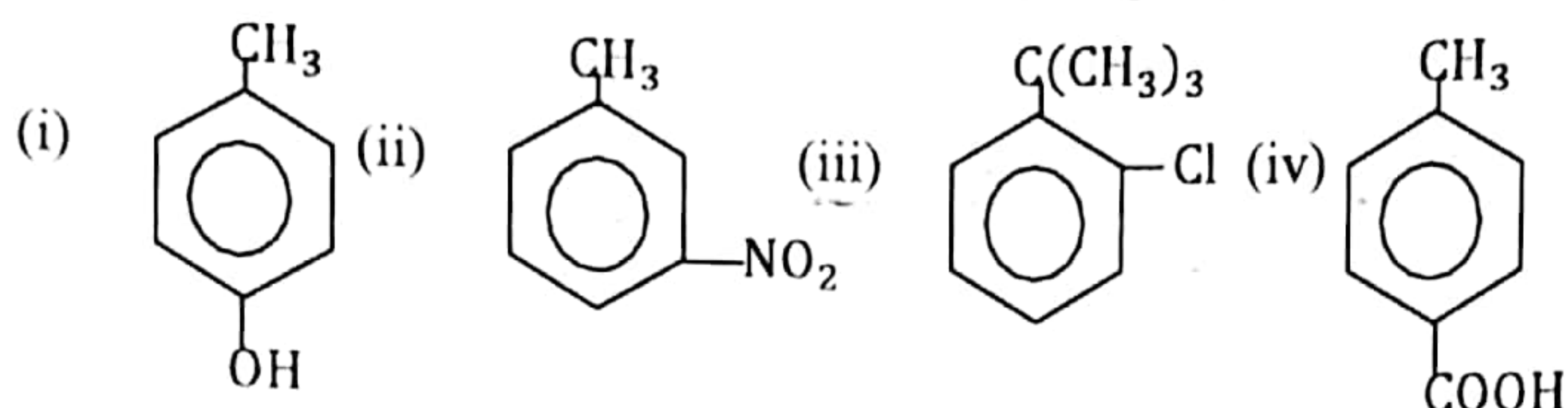
Write structural formula of main substitutional product in the followings organic reactions.





Example 3

Which of substituent entered first in the following organic compounds? Give reasons for your choice.



i) Either of the two (OH or CH₃) substituents entered first.

Reason:

In a given compound OH and CH₃ are para related and both OH and CH₃ are ortho-para directors and hence either of the two can be entered first so as to direct the incoming substituent at para position.

ii) NO₂ entered first

Reason:

In a given compound NO₂ and CH₃ are meta related, so NO₂ being meta director must be entered first so as to direct CH₃ (ortho-para director) at meta position.

iii) Cl entered first

Reason:

In a given compound C(CH₃)₃ and Cl are ortho related and both C(CH₃)₃ and Cl are ortho-para directors. C(CH₃)₃ having larger size forms para product as major product (as result of its large steric hindrance) while Cl being smaller in size exerts lower steric hindrance therefore has greater probability of forming ortho product and hence Cl must be entered first so as to direct OH at ortho position.

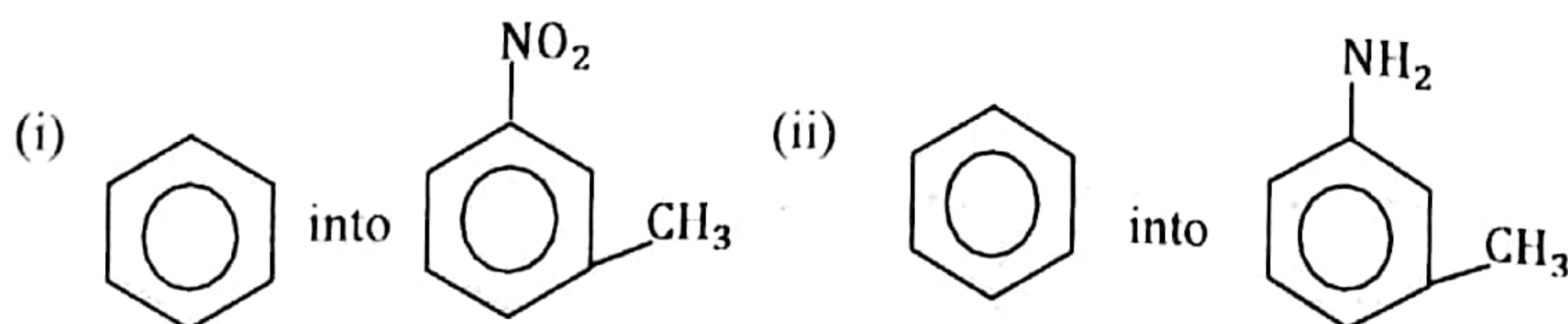
iv) CH₃ entered first.

Reason:

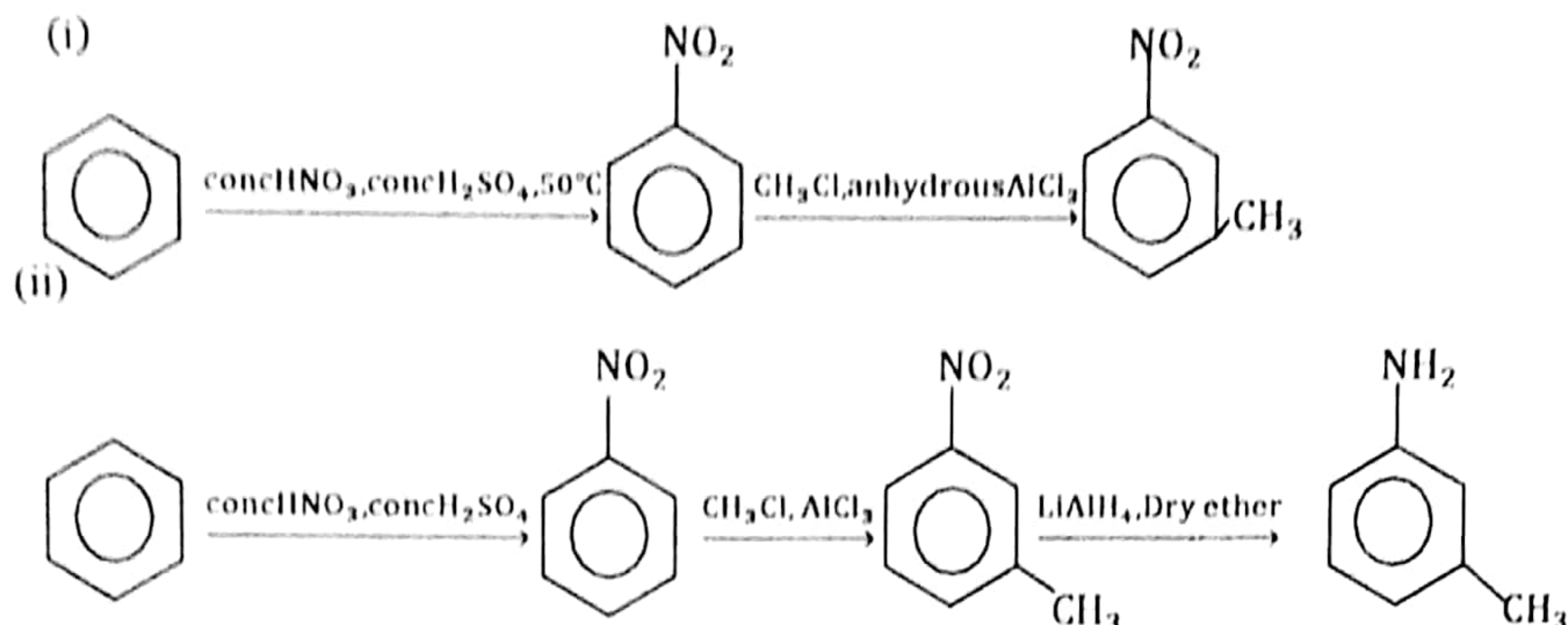
In a given compound CH₃ and COOH are para related; CH₃ being ortho-para director must be entered first so as to direct incoming COOH at para position.

Example 4

Show how the following conversions can be achieved.



Solution

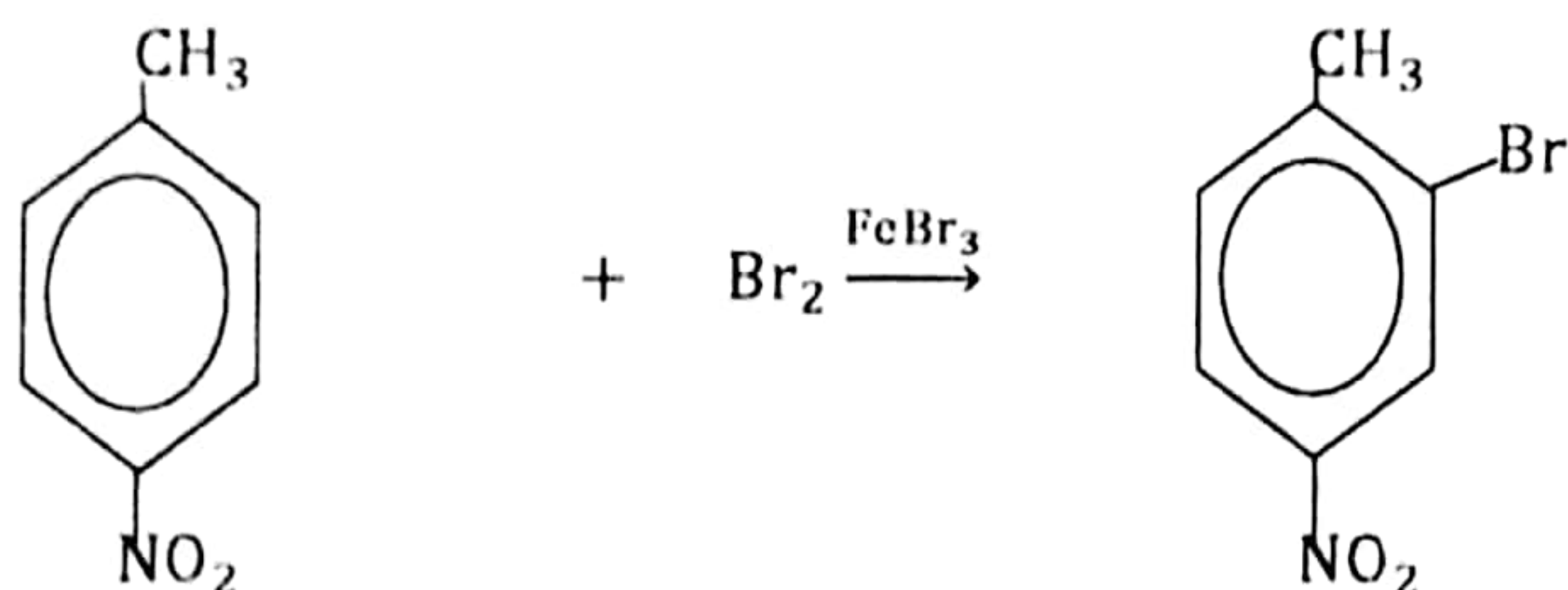


THIRD SUBSTITUTION IN BENZENE

For benzene ring which has already two substituent groups, the following general rules are useful in doing **third substitution**:

Rule 1:

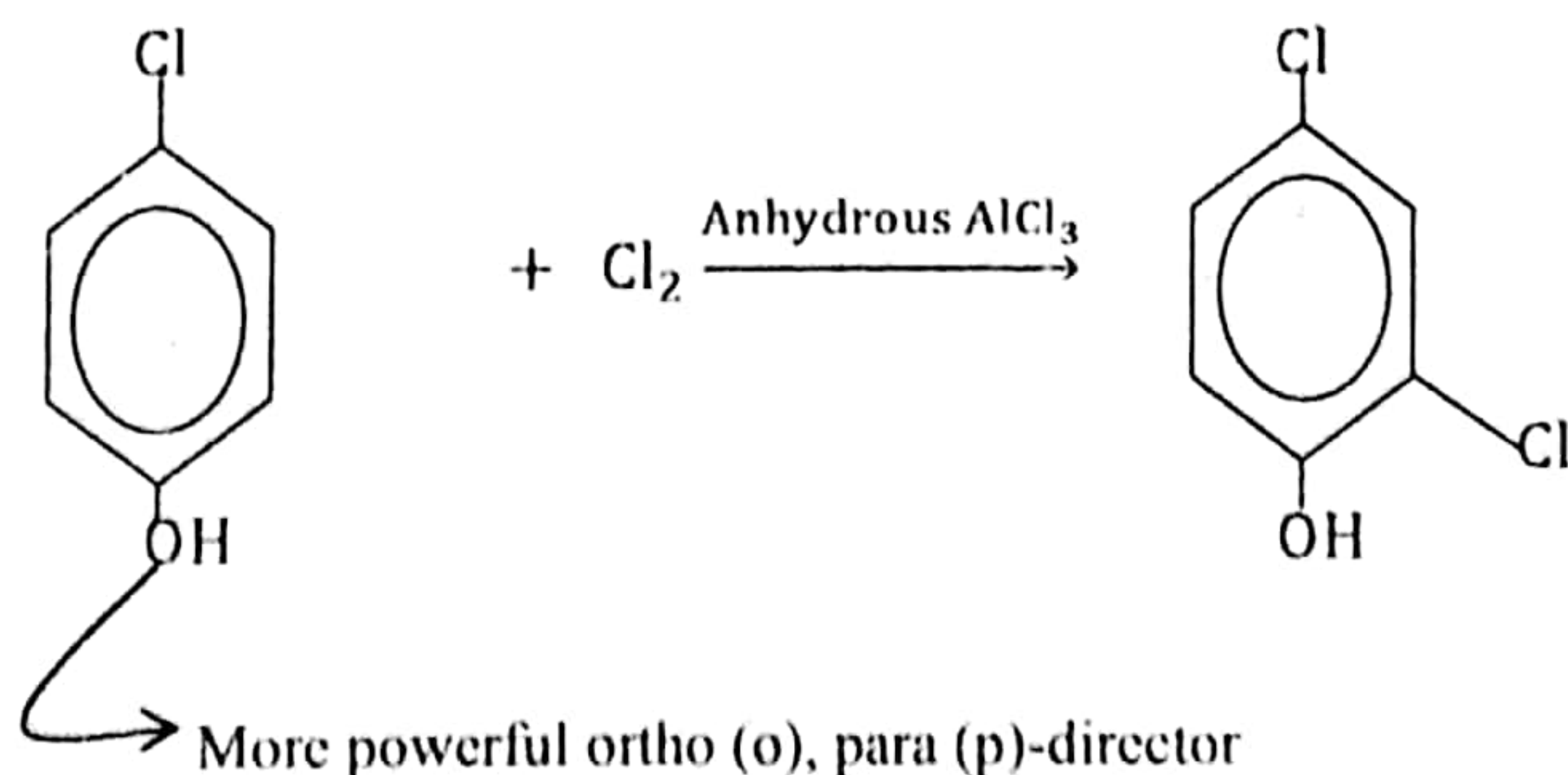
If two substituent groups direct an incoming group at the same position, that will be the principal position of the third substitution.



(Br attach to carbon which is ortho position to CH_3 and it is also meta position to NO_2)

Rule 2:

If two groups conflict (compete) in their directive effects, the more powerful activator will exert the predominant directive effect and will determine the position of incoming electrophile.

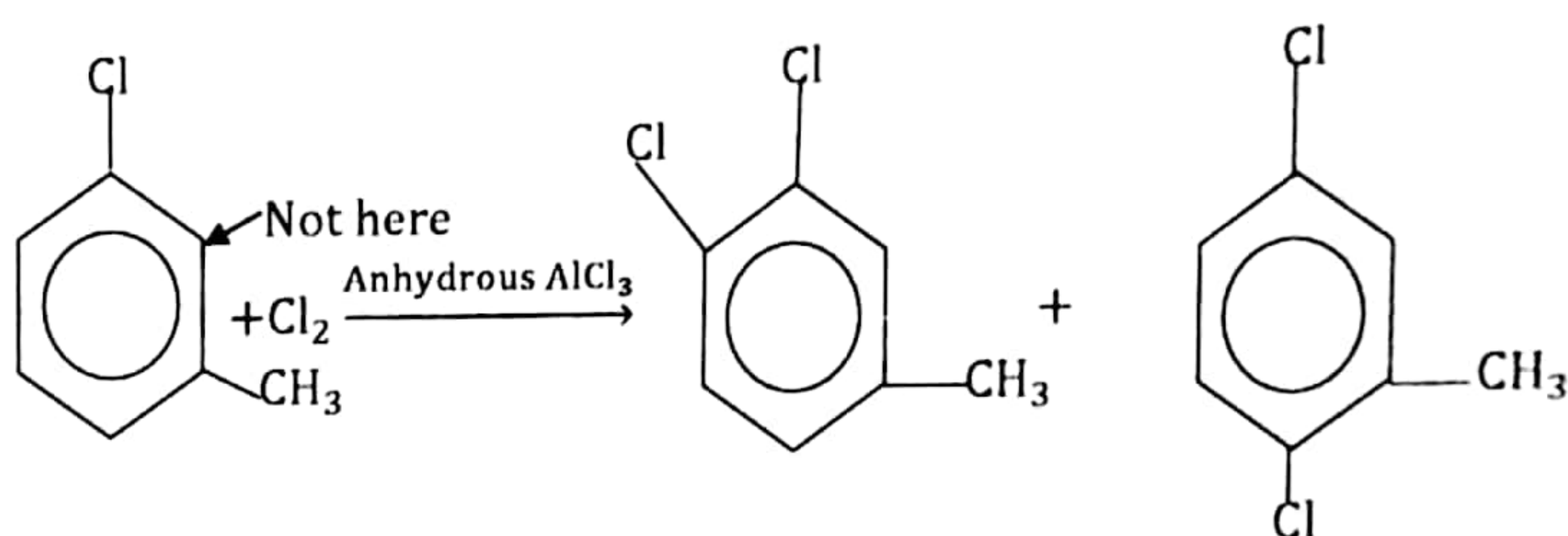


Thus if activator and deactivator compete in their directive effects, the activator will determine the position of incoming electrophile.

The following table is useful in choosing more powerful activating group:

o,p - directors	m-directors (All deactivating)
INCREASING ACTIVATION ↑ $-\text{NH}_2, -\text{NHR} - \text{NR}_2$ $-\text{OH}$ $-\text{OR}$ $-\text{NH} - \text{CO} - \text{R}$ $-\text{C}_6\text{H}_5$ (aryl) $-\text{R}$ (alkyl) $-\text{X}$ (deactivating)	$-\text{COR}$ $-\text{COOR}$ $-\text{SO}_3\text{H}$ $-\text{CHO}$ $-\text{COOH}$ $-\text{CN}$ $-\text{NO}_2$ $-\text{NR}_3^+$ ↓ INCREASING DEACTIVATION

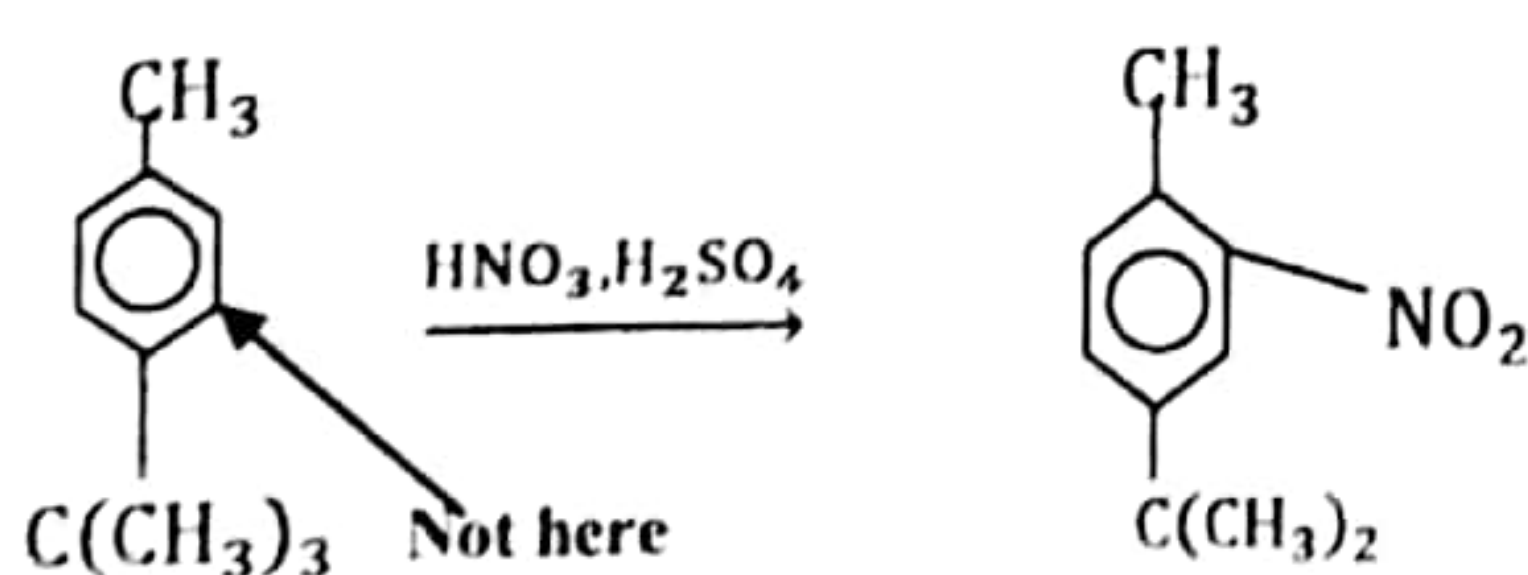
Rule 3: If two groups on a ring are meta to each other, the ring does not usually undergo substitution at the position between them, even if the ring is activated. The lack of reactivity at this position is due to steric hindrance.



Rule 4:

If two substituents have similar activating effects and each direct incoming electrophile to its respective ortho position then the smaller substituent will determine the major product. This is because; the smaller substituent exerts weaker steric effect (hindrance).

For example:



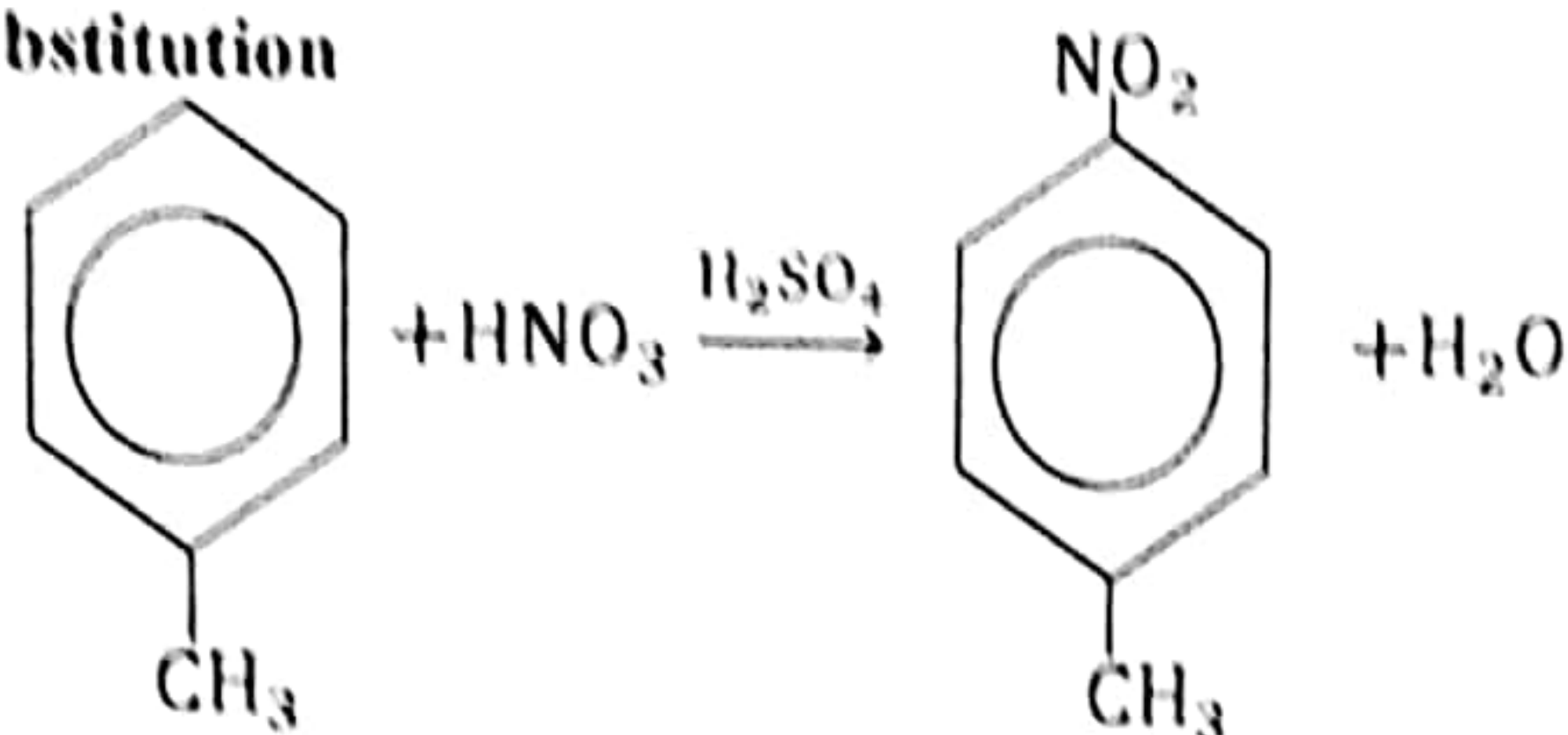
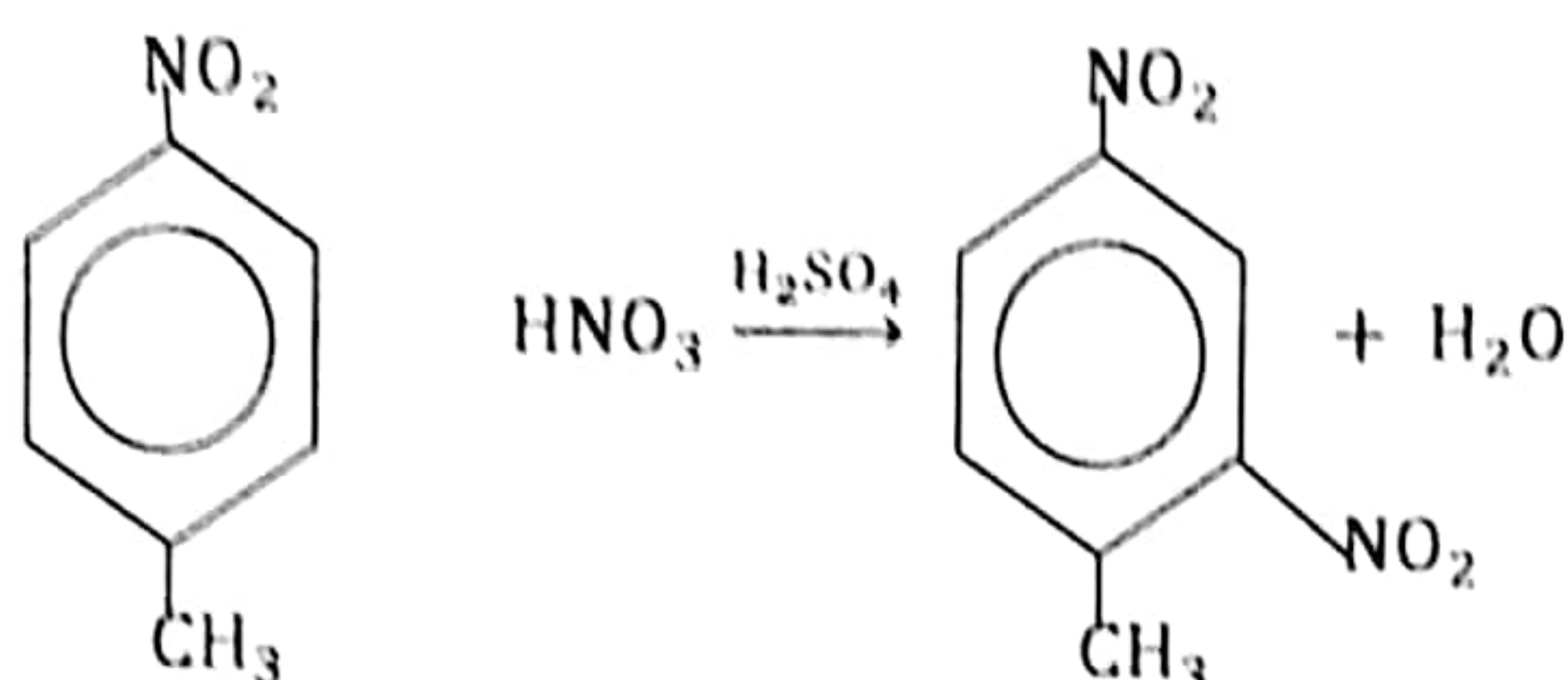
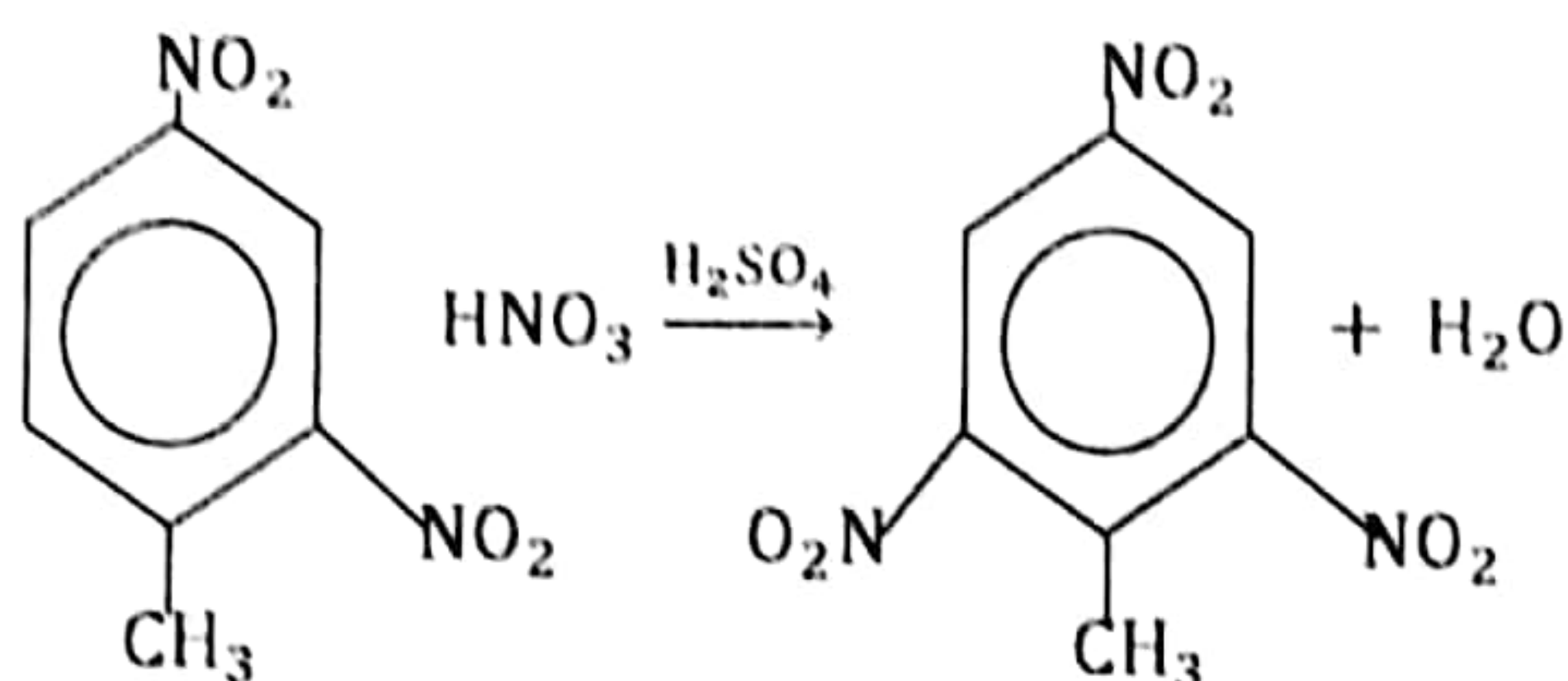
Rule 5:

If two deactivating groups are on the ring, regardless of their positions, it may be difficult for the third substitution to occur.

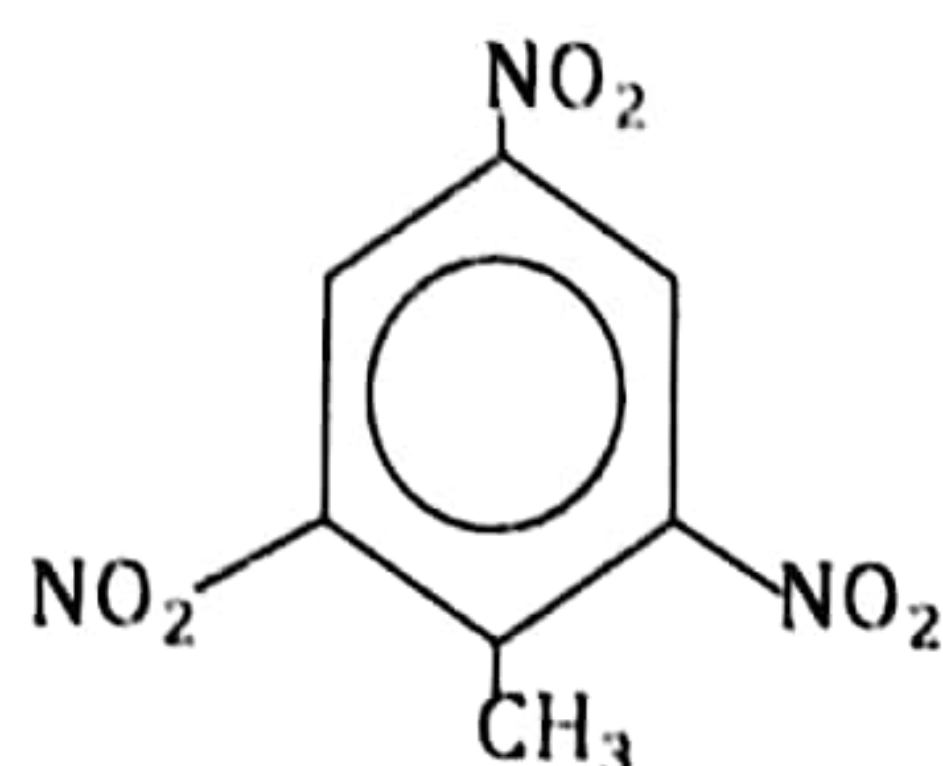
Example 5

The explosive TNT (trinitrotoluene) can be made by nitrating toluene with mixture of nitric and sulphuric acids,

- Considering the orientation effect of various groups suggest the correct structure of TNT
- Condition for the reaction must be made gradually more severe as the nitration proceeds. Explain why?

Solution**First substitution****Second substitution****Third substitution**

Hence the structure of TNT is

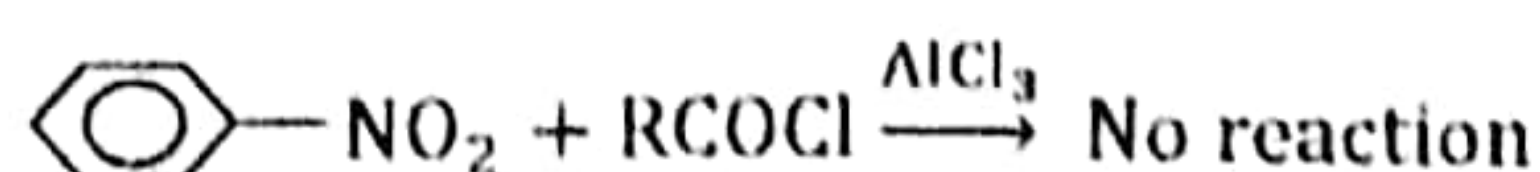


- (iii) As the number of NO_2 groups which are strong deactivating groups increases, it becomes more difficult to affect more substitution in the benzene ring thus requiring higher and higher temperature (more severe conditions) as the reaction proceeds so as to allow the substitution reaction to proceed (through increasing the rate of reaction).

Little care is needed: Most of students talk about steric hindrance as the cause of applying severe conditions. That is not correct because steric hindrance is significant if the electrophile is attached to carbon lying between two carbons with substituents; and in the case of formation of TNT there is no such situation. So actually, steric hindrance is very minor factor in this case.

Last important point to finish with directing effect of substituents in benzene!

A benzene ring deactivated by meta directors (remember; all meta directors are strong deactivators) is not strong nucleophilic enough to undergo Friedel-Craft reaction. For example;



PRACTICE EXERCISE 15

Problem 1

Discuss how methoxy group in anisole, acts as ortho–para director under the following headings:

- Position of carbanion
- Stability of intermediate carbenium ion

Problem 2

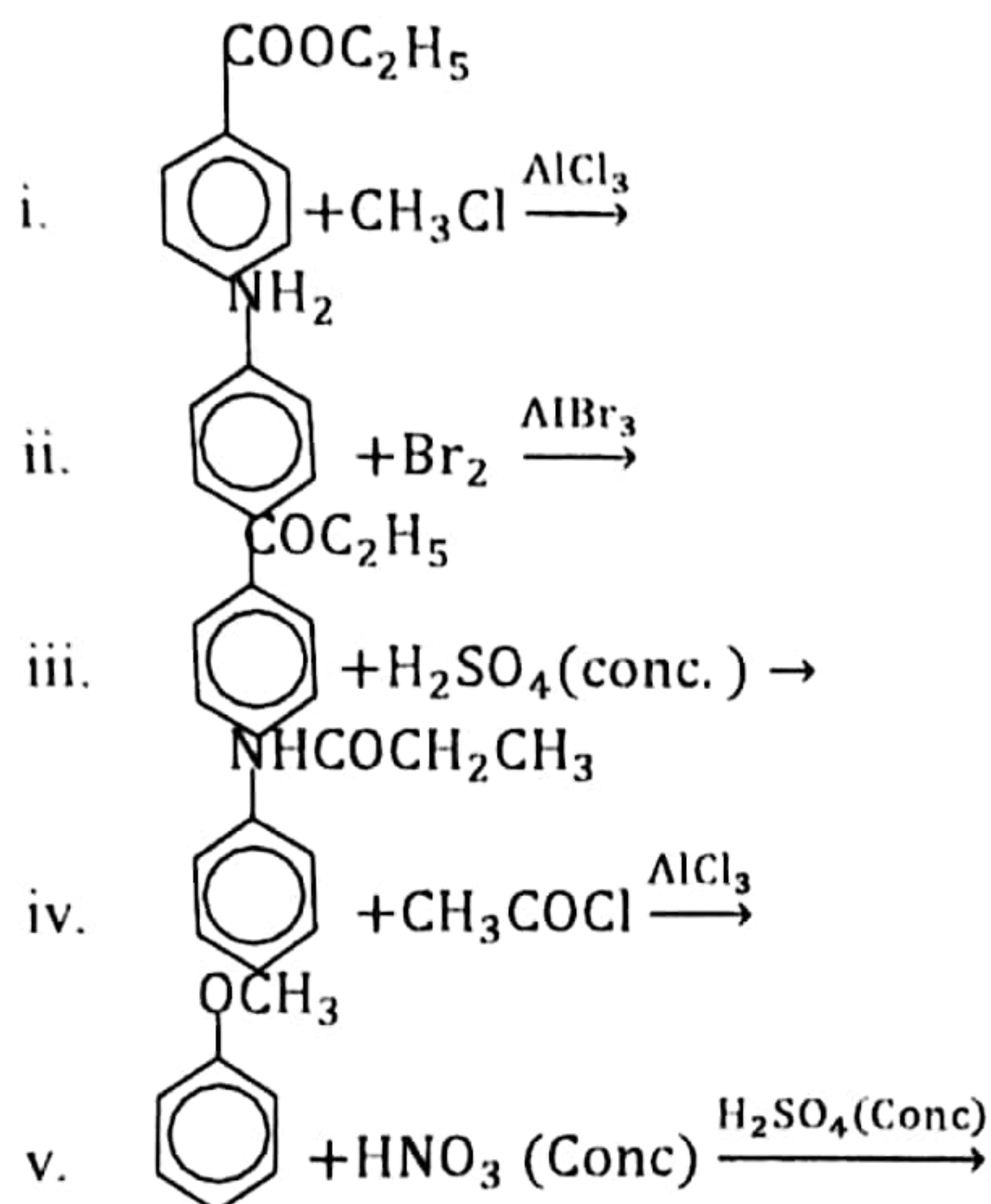
Explain clearly how isopropyl group in cumene directs incoming electrophile at ortho and para positions.

Problem 3

Give clear account for the following statement “Although Cl in chlorobenzene is deactivator, methylation of the chlorobenzene give significant amount of 2-chlorotoluene and 4-chlorotoluene”

Problem 4

Complete the following organic reactions:



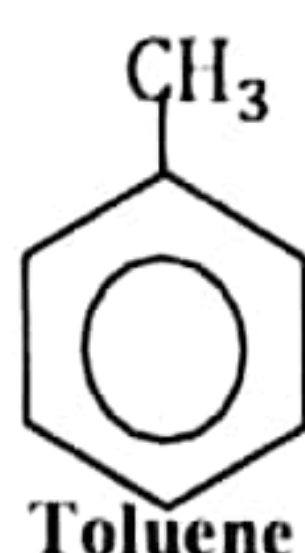
Problem 5

Juma did a mistake in naming a certain organic compounds by naming as tribromophenol. The mistake lies in the fact that he forgot to indicate position of substituent in the compound. If the compound can also be formed from bromination of phenol; by considering directing effect in the benzene, suggest the structure of the compound and hence give its correct IUPAC name

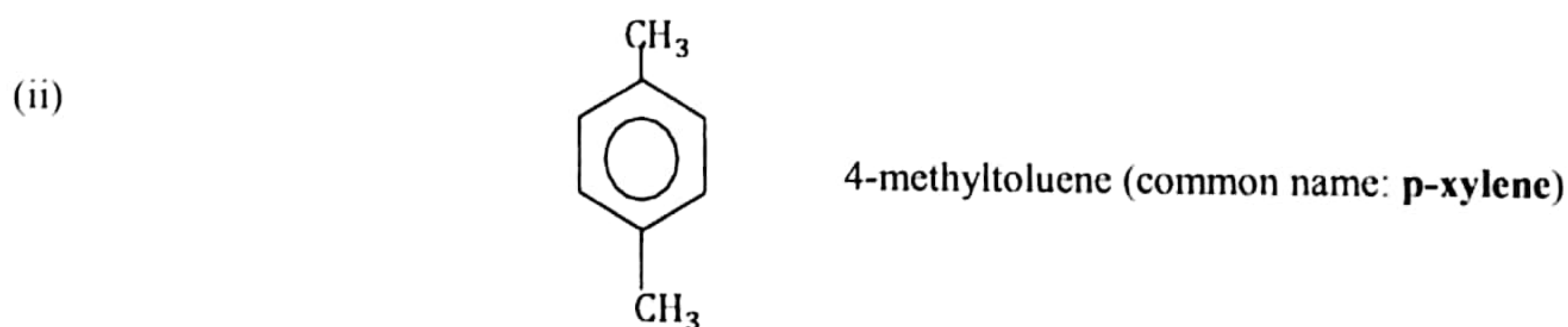
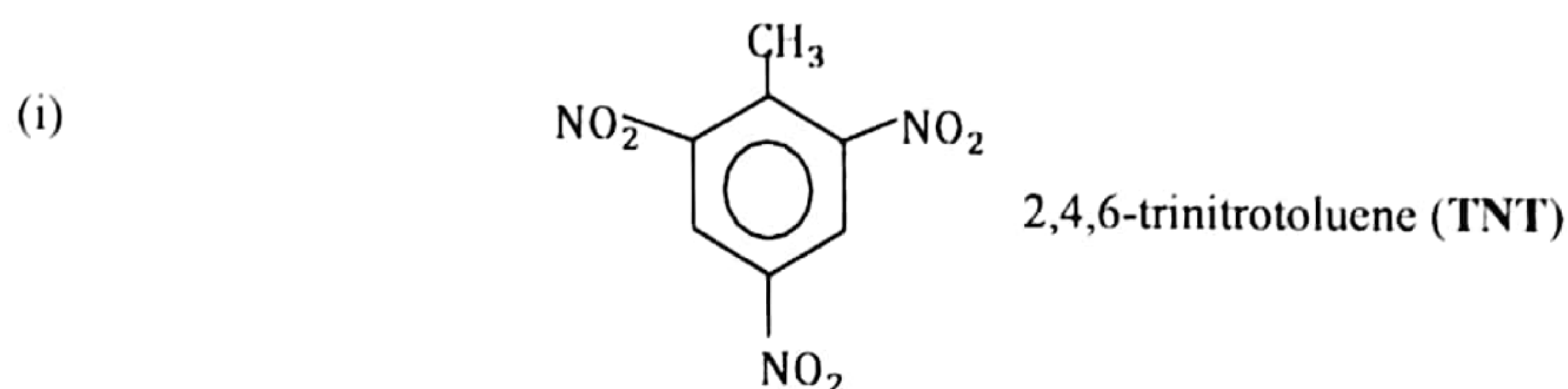
Chapter 16

TOLUENE

Toluene (IUPAC name is methylbenzene) is an aromatic compound which is formed when one mole of hydrogen atom of benzene is replaced by methyl group.



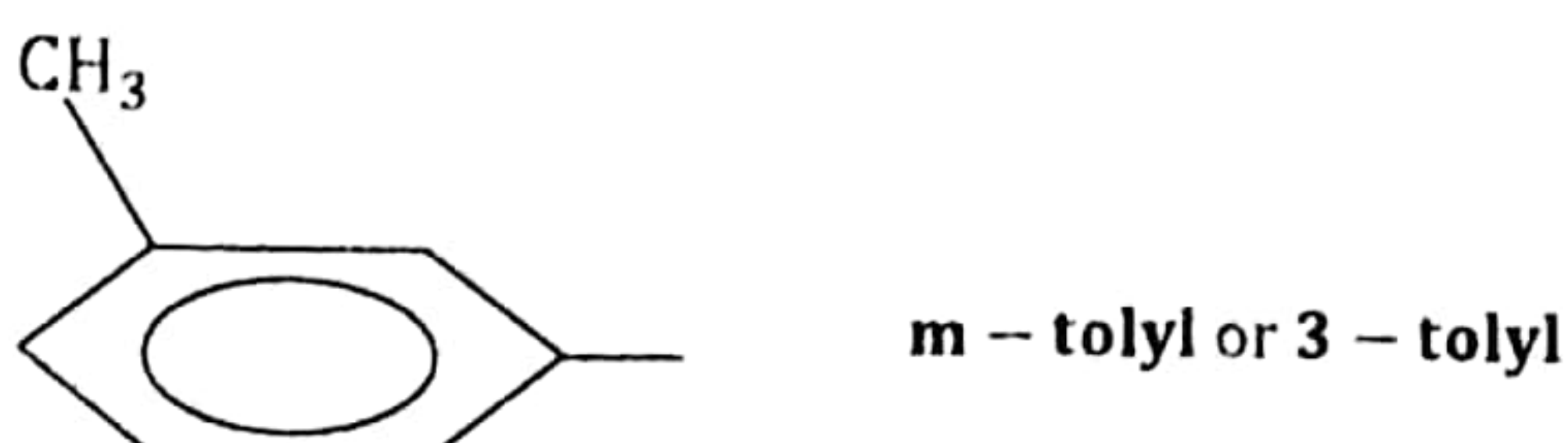
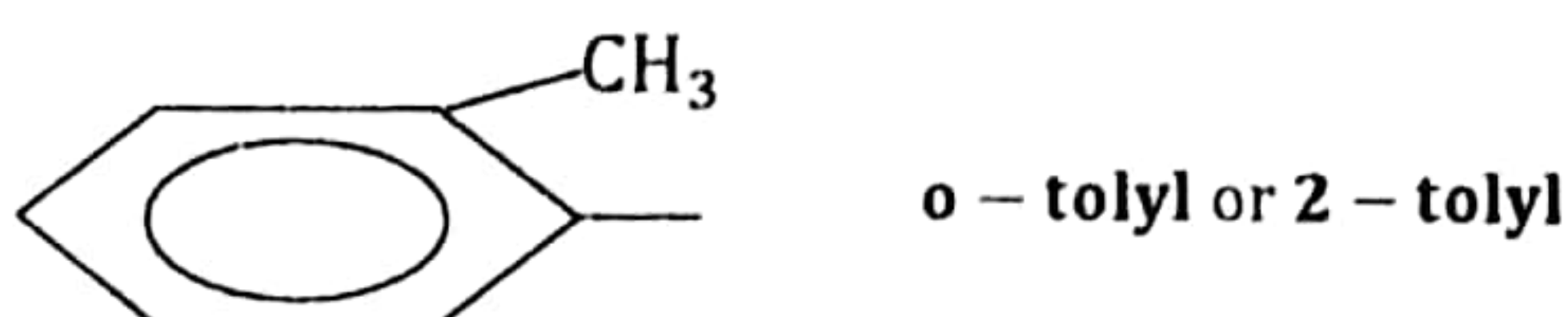
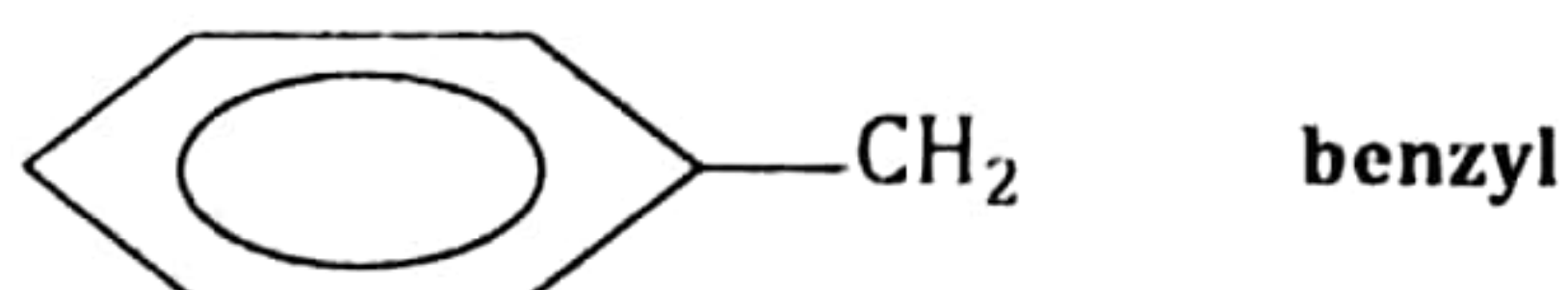
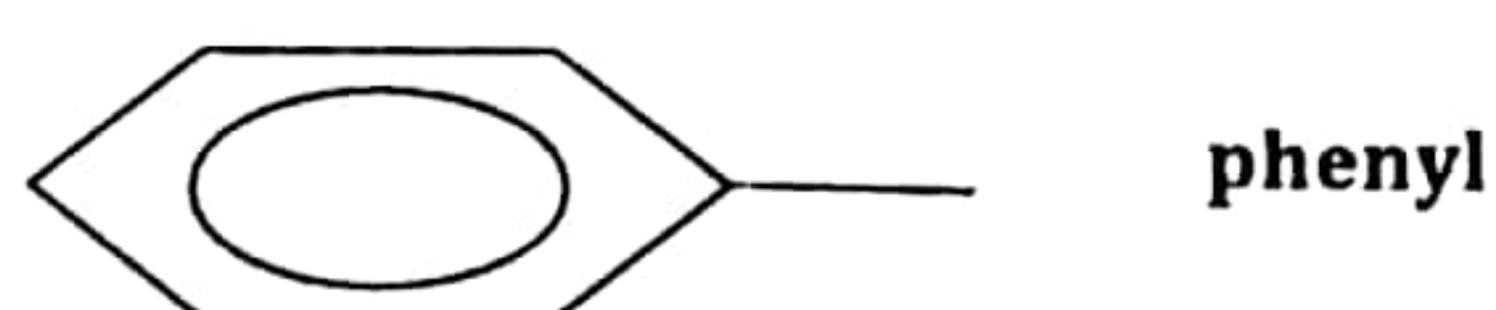
With substituents which are less dominant than alkyl groups or other alkyl groups themselves, compounds with methyl group can be named as derivative of toluene. For example:

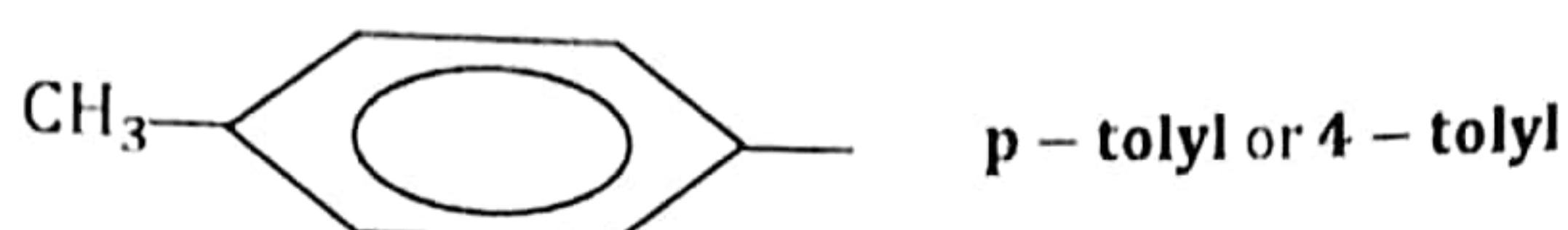


In (ii) above, 'p' stands for para. If the two methyl groups would be meta related then the common name would be **m-xylene** and if would be ortho related, the name would be **o-xylene**.

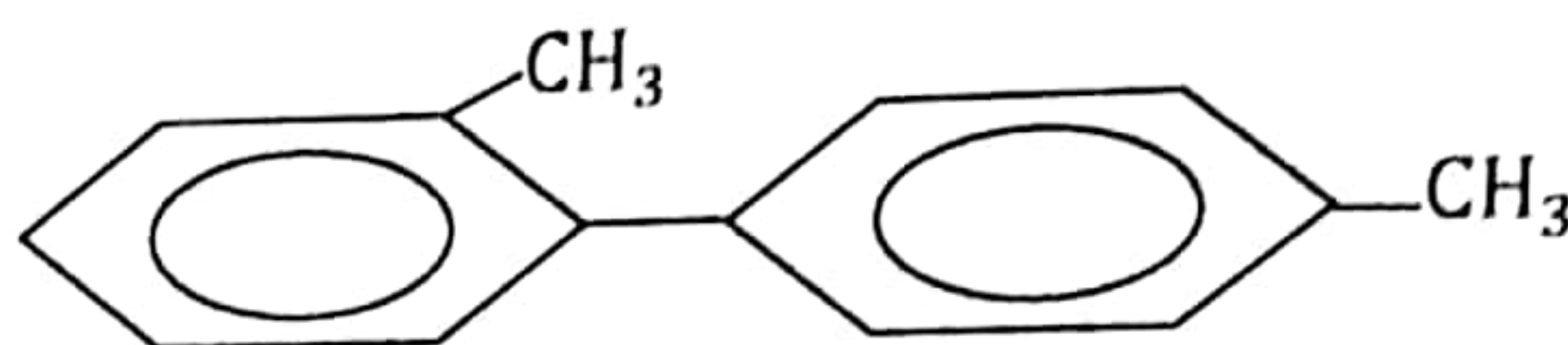
It is worth to understand that:

Benzene as a substituent (with molecular formula C_6H_5) is called **phenyl group**. But naming of toluene as the substituent depends on the point of attachment.





For example, the following compound;



is named as 2-(p-tolyl)toluene or 2-(4-tolyl)toluene

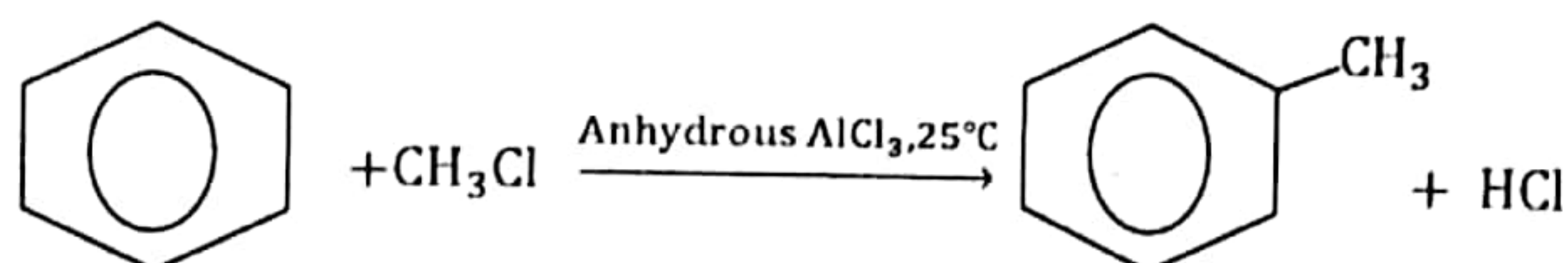
It should be noted that:

Substituent groups with at least one benzene ring are termed as **aryl groups**.

PREPARATIONS OF TOLUENE

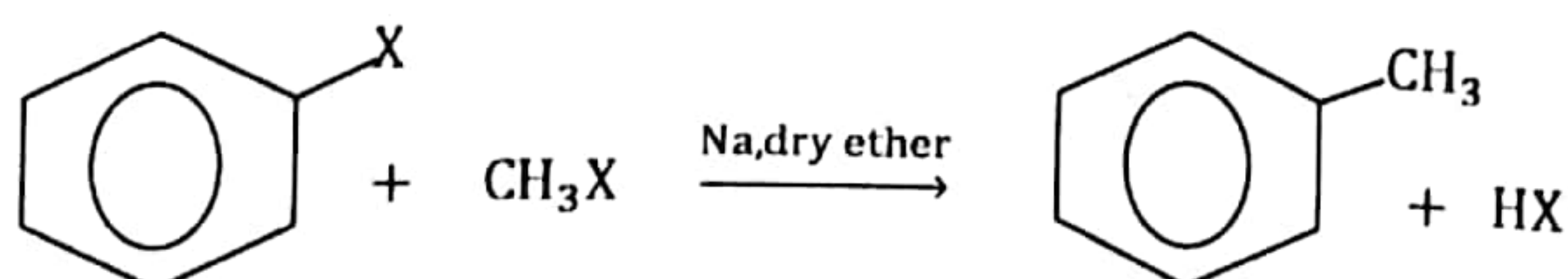
Methylation of benzene

Benzene reacts with halomethane under presence of lewis acid giving toluene. For example;

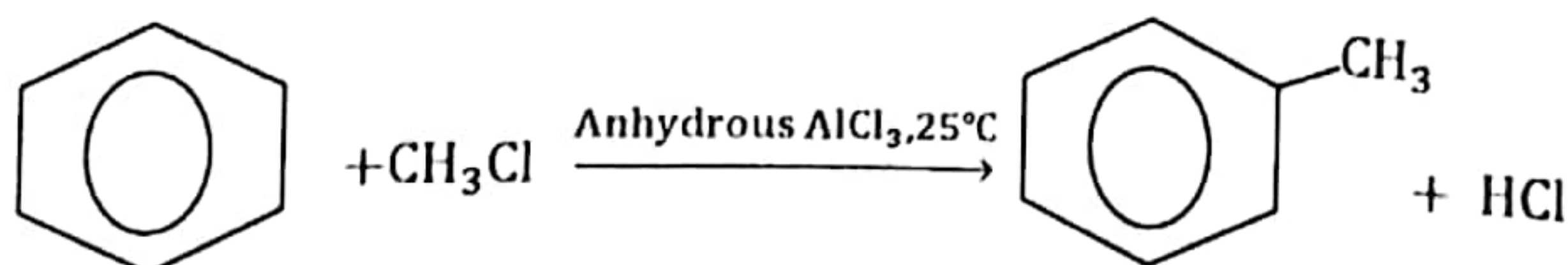


Reaction between halobenzene and halomethane under presence of sodium and dry ether

Generally;



For example:



PHYSICAL PROPERTIES OF TOLUENE

- It is colourless liquid at room temperature
- It is denser than water
- Its vapour density is larger than that of the air
- It is soluble in non polar solvents like organic solvent (toluene itself is good organic solvent)
- It melts at temperature of -95°C and boils at 111°C

Note:

In most cases toluene is used as organic solvent instead of benzene because it is less toxic.

CHEMICAL RECTIONS OF TOLUENE

Commonly toluene undergoes the following chemical reactions:

- Side chain chemical reactions
- Electrophilic substitution reactions in benzene ring

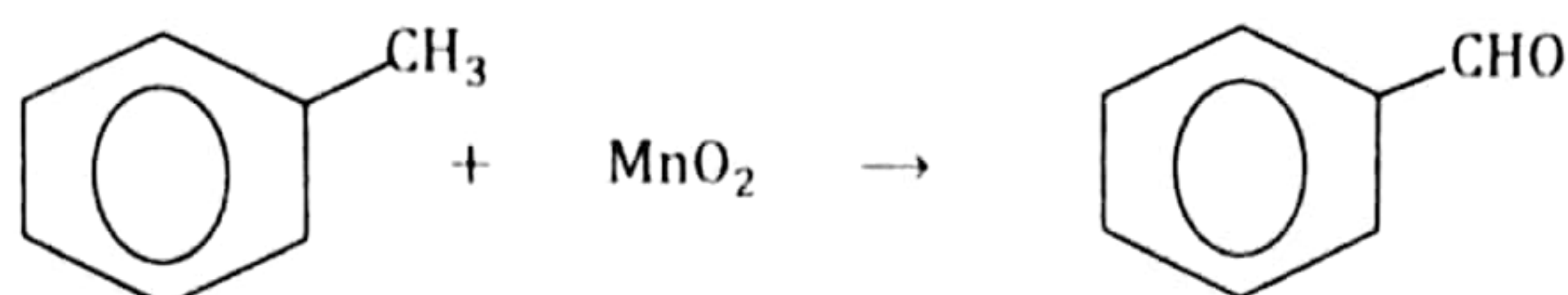
Side chain chemical reactions

Under this heading toluene undergoes the following chemical reactions;

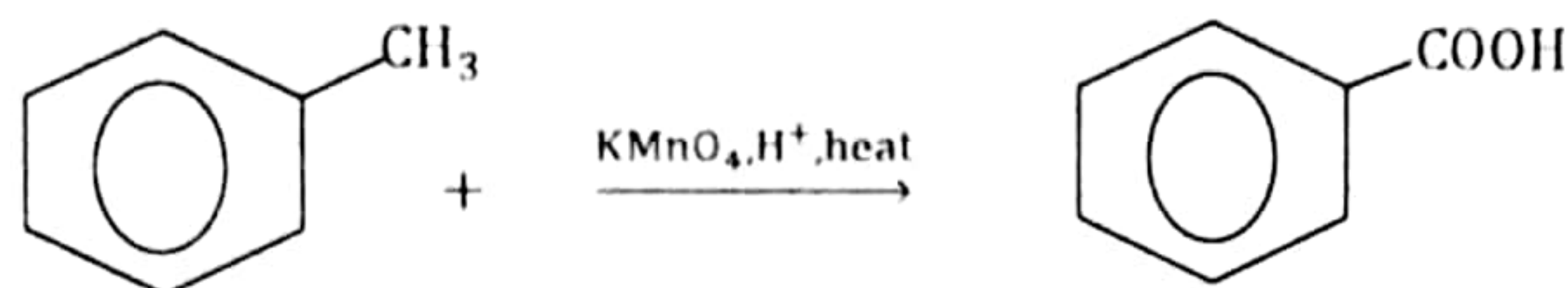
- Oxidation
- Free radical substitution reactions

Oxidation

With milder oxidizing agent like MnO_2 , benzaldehyde is formed.



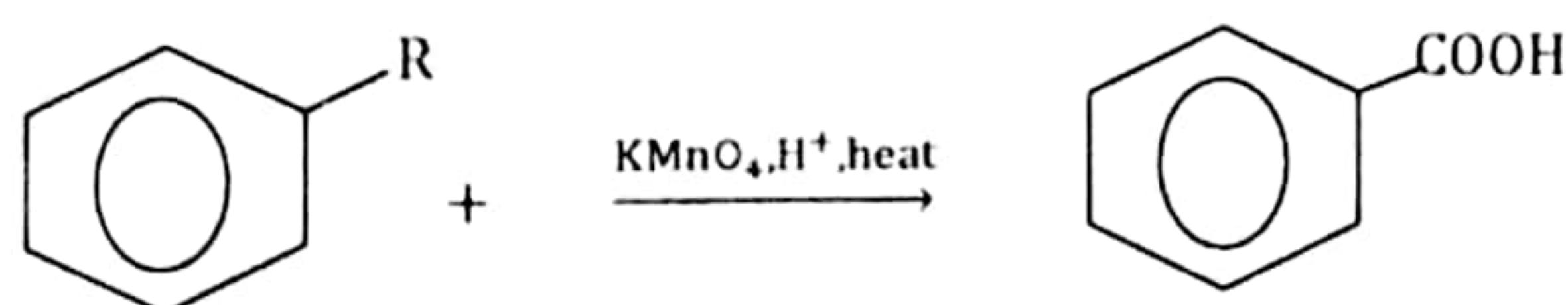
But with strong oxidizing agent like KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, benzoic acid is formed.



Generally;

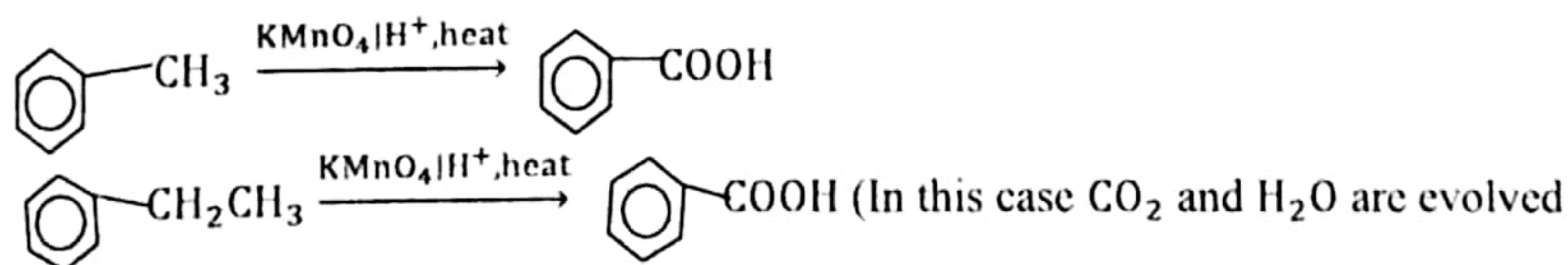
The side chains of alkyl benzenes (not necessary for the side chain to be methyl group) are oxidised by strong oxidizing agents such as hot acidified potassium permanganate.

That is;



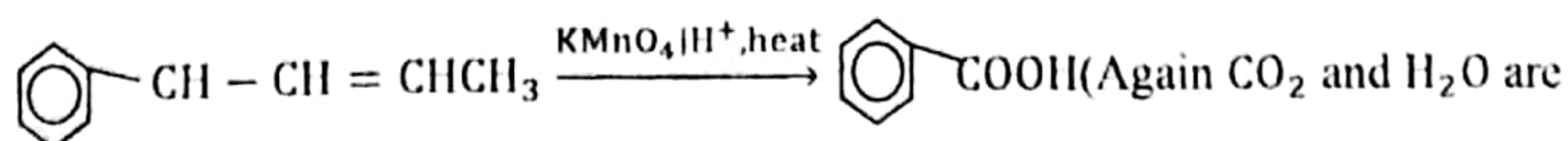
Where R is any group of aliphatic hydrocarbon

- The oxidation takes place at benzyl carbon (carbon which is directly bonded to benzene), so **regardless to the number of carbons in the side chain all alkyl benzenes are oxidised to benzoic acid.**



as byproduct)

Similarly;



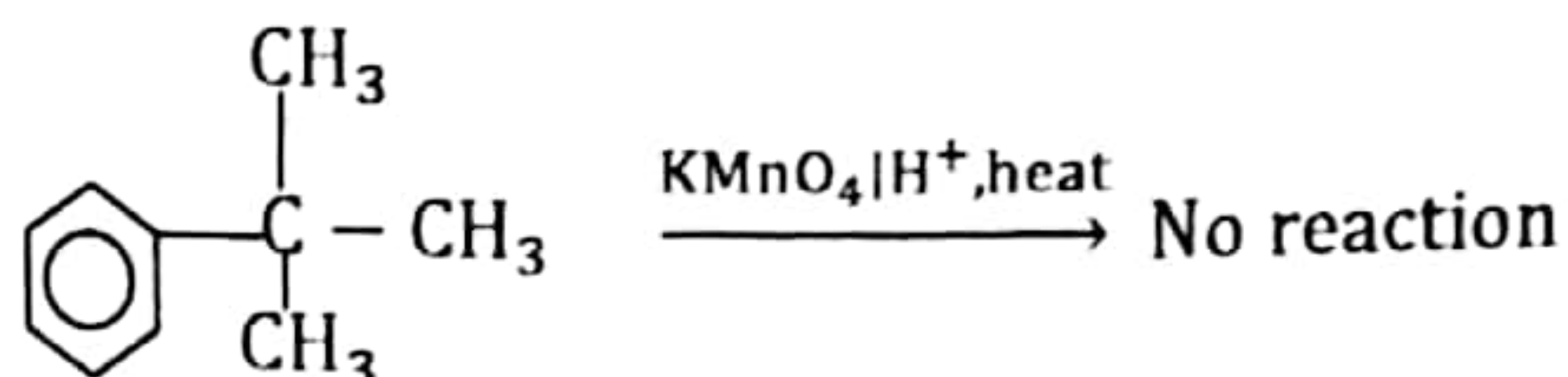
byproduct)

Here don't confuse with the reaction occurring at $\text{C}=\text{C}$ of the side chain. The oxidation of benzyl carbon is preferred to the reaction at $\text{C}=\text{C}$.

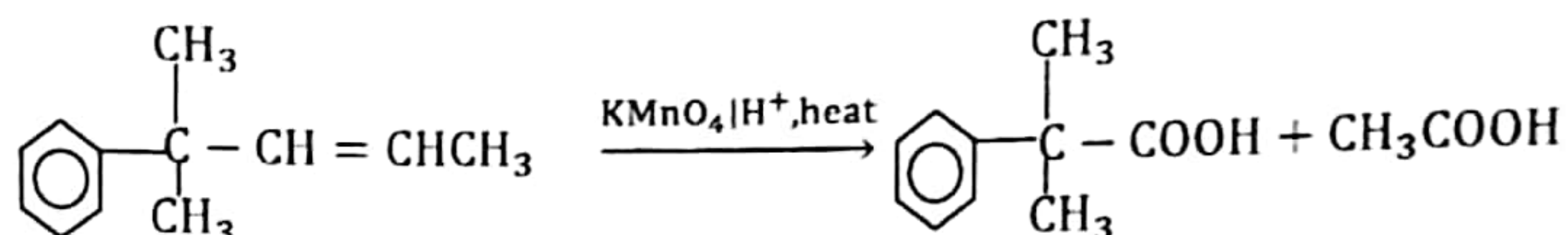
Attention!

Since the reaction (oxidation) starts at benzyl carbon, presence of removable hydrogen at benzyl carbon is necessary for the oxidation to occur. If there is no hydrogen at benzyl carbon the reaction will not occur.

For example;



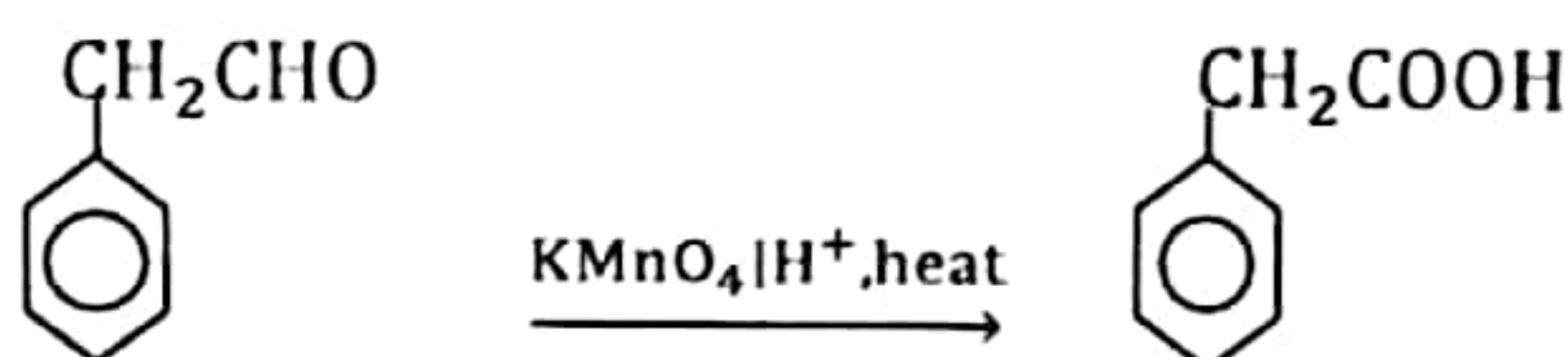
But;



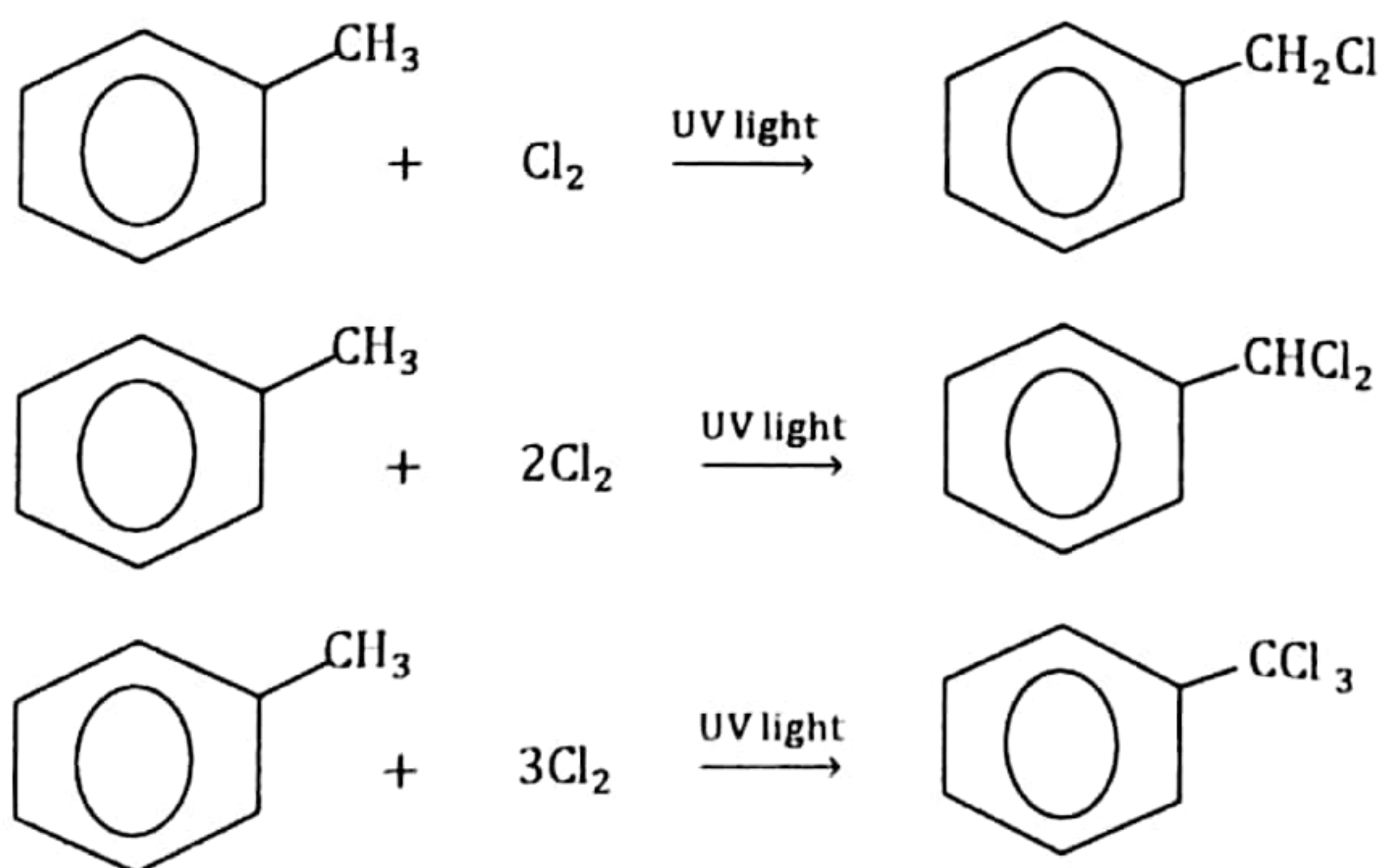
(Here presence of $\text{C}=\text{C}$, allows the oxidation to occur at this double bond although there is no hydrogen at benzyl carbon).

However!

Because aldehyde group is very powerful reducing agent, if the side chain contain the aldehyde group the reaction occurs to this group and not to the benzyl carbon. For example;

**Free radical substitution reactions**

With halogens under presence of UV or very high temperature, toluene tends to undergo side chain free radical substitution reactions.

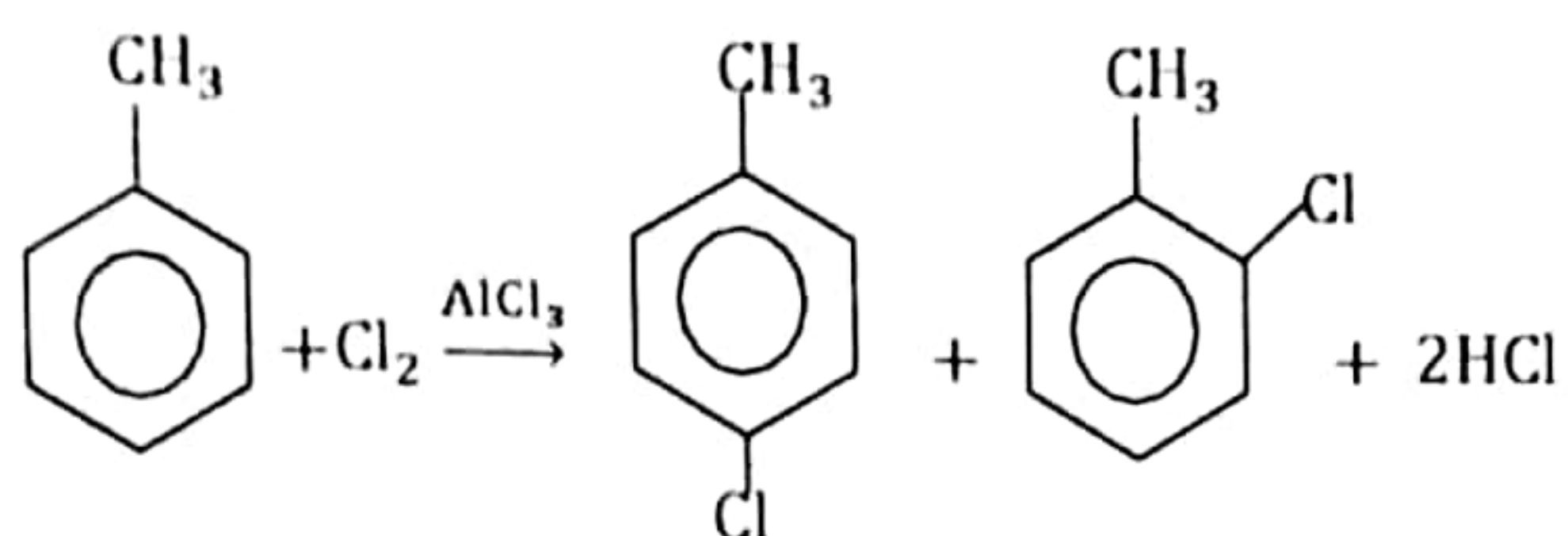
**Electrophilic substitution reactions**

Under this heading toluene undergo similar chemical reactions as those of benzene.

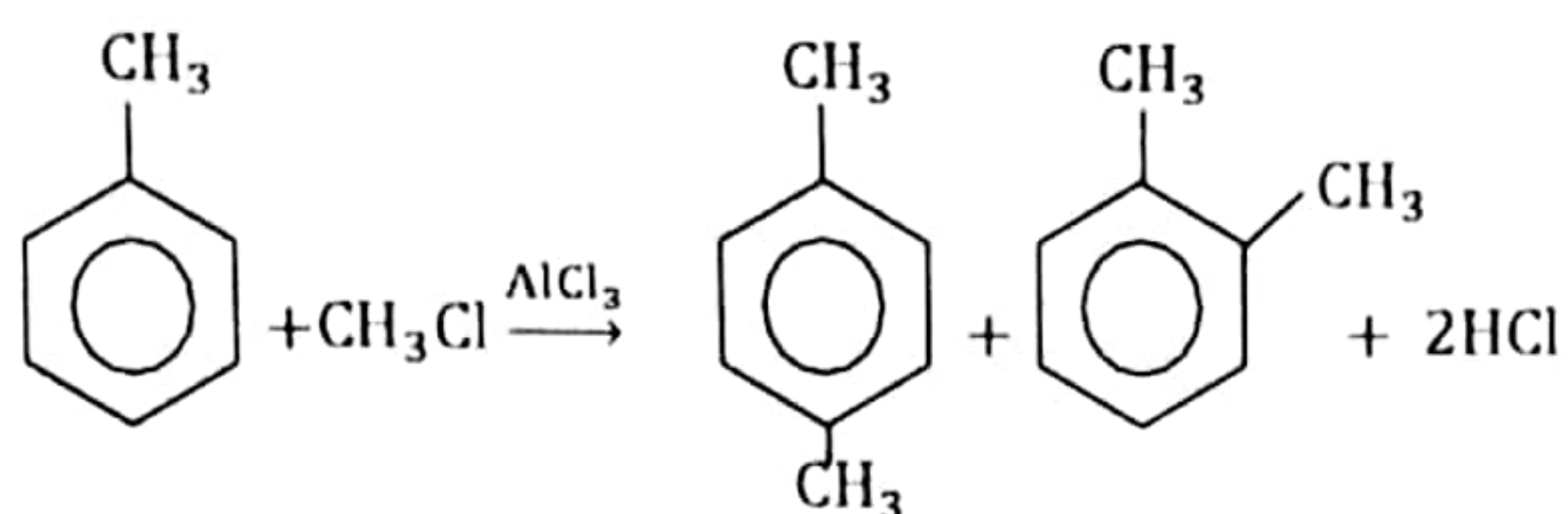
- The only modification on the reaction is that; methyl group in toluene acts as ortho-para director.
- Also methyl group being activator makes toluene more reactive than benzene towards electrophile. Thus electrophilic substitution reactions in toluene occur at faster rate than in benzene.

Examples of electrophilic substitution reactions of toluene are;

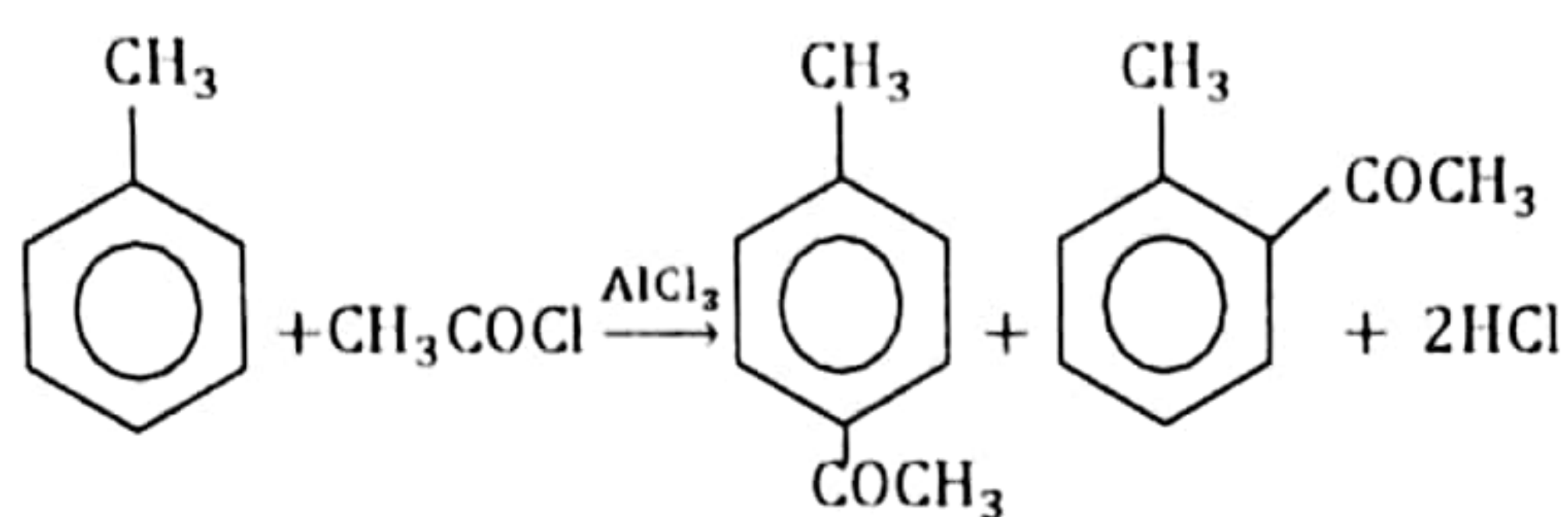
Halogenation



Alkylation



Acylation



The student should be able to give other examples of electrophilic substitution reaction (refer to electrophilic substitution in benzene).

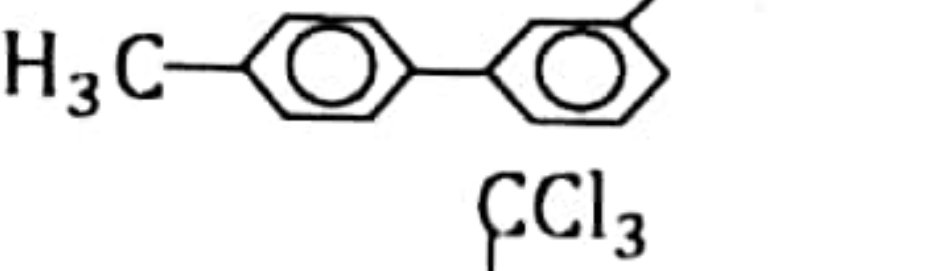
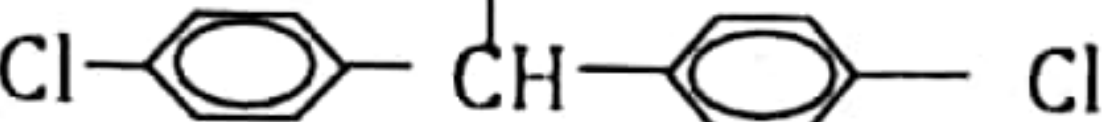
PRACTICE EXERCISE 16

Problem 1

Name all aromatic isomers of the organic compound with molecular formula of C_8H_{10}

Problem 2

Give IUPAC names of the following organic compounds

- i. 
- ii. 
- iii. 

Problem 3

Give commercial names of:

- i. Methylbenzene
- ii. 2-methyltoluene
- iii. 3-methyltoluene
- iv. 2,4,6-trinitrotoluene

Problem 4

Write down chemical equation to show preparation of toluene from:

- i. Benzene
- ii. Bromobenzene
- iii. Sodium ethanoate
- iv. Benzaldehyde

EXAMINATION QUESTIONS-1

Question 1

- (i) Explain why phenylamine is a weaker base than ethylamine.
- (ii) Suggest why ethanamide, CH_3CONH_2 , is a weaker base than ethylamine.

Question 2

Explain why ethylamine is a stronger base than ammonia.

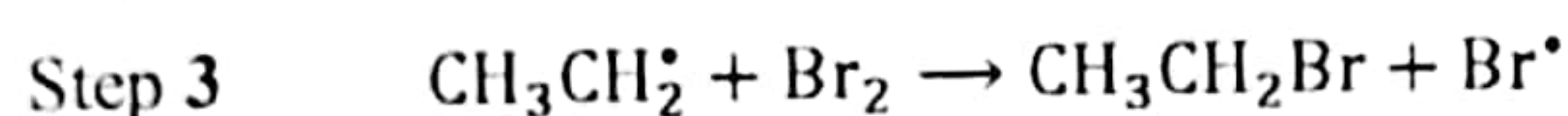
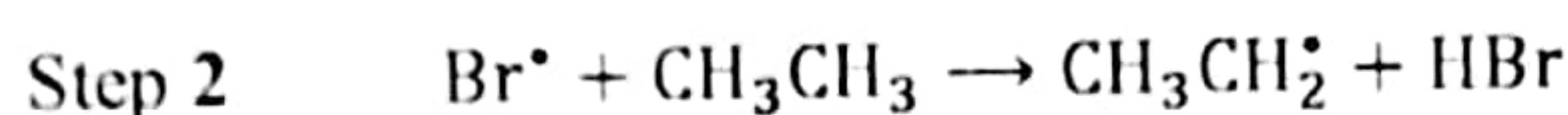
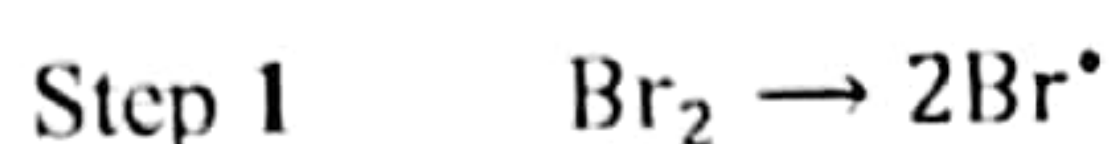
Question 3

Crude oil is a complex mixture of compounds. Most of these are hydrocarbons although there are also sulphur compounds present. Some of the hydrocarbon fractions of crude oil are catalytically cracked.

- (i) What is the economic importance of cracking?
- (ii) The alkane, $\text{C}_{14}\text{H}_{30}$, can be cracked to give an alkene and an alkane. Write a balanced equation to show one way in which this could happen.

Question 4

The reaction of bromine with ethane is similar to that of chlorine with ethane. Three steps in the bromination of ethane are shown below.



- (a)
 - (i) Name this type of mechanism.
 - (ii) Suggest an essential condition for this reaction.
 - (iii) Steps 2 and 3 are of the same type. Name this type of step.
 - (iv) In this mechanism, another type of step occurs in which free-radicals combine. Name this type of step. Write an equation to illustrate this step.

Question 5

Alkanes and alkenes differ strikingly in their reactivity, for example with chlorine; this is a consequence of their structure.

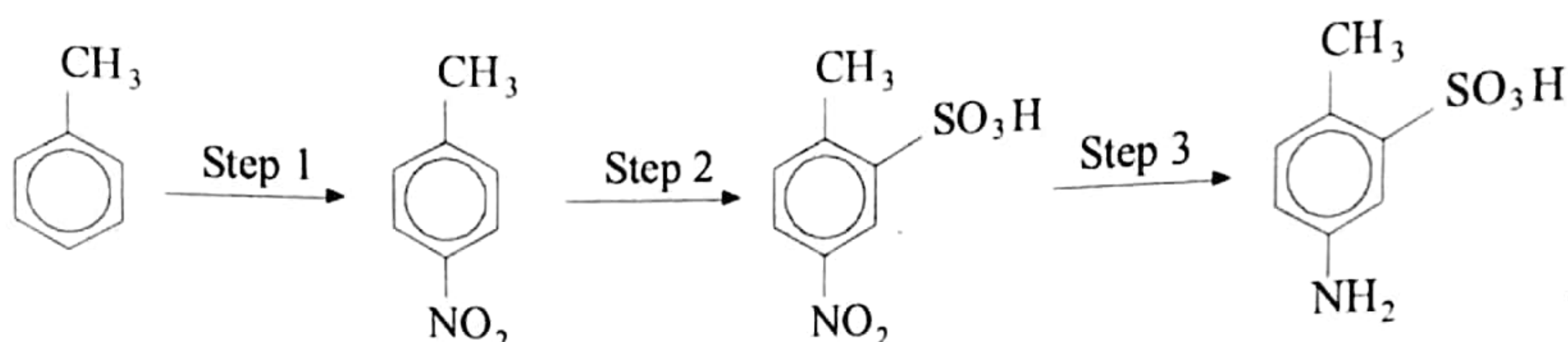
- (a)
 - (i) Give the equation for the reaction of one mole of ethane with one mole of chlorine.
 - (ii) Butane is a by-product by this reaction. How does it arise?
- (b)
 - (i) Give the equation for the reaction of chlorine with ethene.
 - (ii) Explain in terms of their structures why the reactions of ethane and of ethene with chlorine are so different.
 - (iii) Why are alkenes not used as fuels?

Question 6

- a) Benzene reacts with nitric acid in the presence of a catalyst to form nitrobenzene. This is an electrophilic substitution reaction.
 - (i) Write an equation for the overall reaction.
 - (ii) State the name of the catalyst used.
 - (iii) Write the formula, including its charge, of the electrophile involved in the reaction.
- b) Methylbenzene is converted into (chloromethyl) benzene in a free radical substitution reaction. $\text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{HCl}$
 - (i) Write an equation for the initiation step.
 - (ii) Write equations for the two propagation steps.
 - (iii) Give the formula of another possible organic product of the reaction.

Question 7

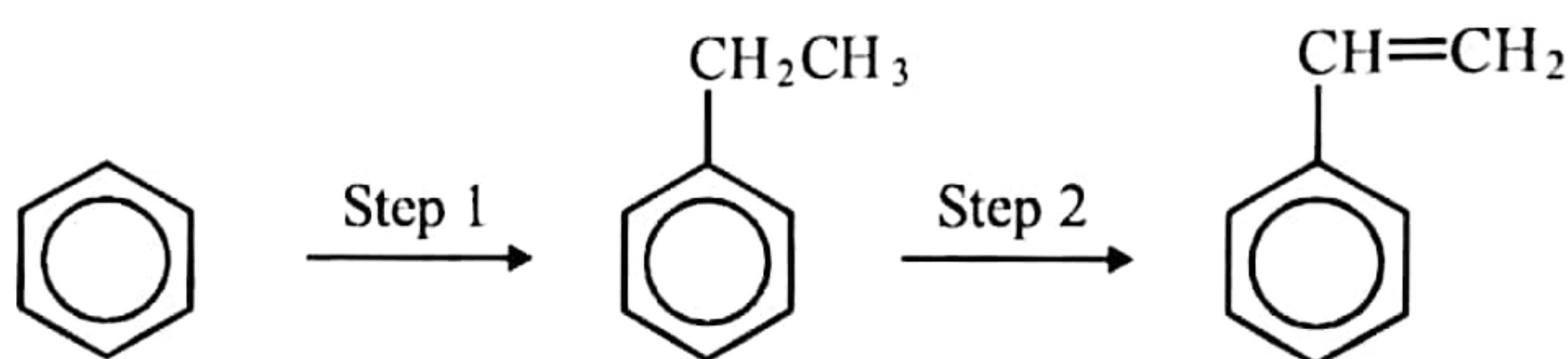
5-Amino-2-methylbenzenesulphonic acid can be obtained from methylbenzene in a three-step synthesis:



name the type of reaction taking place and suggest a suitable reagent or combination of reagents.
 (b) Write an equation for the formation of the reactive inorganic species involved in the mechanism in Step 1.

Question 8

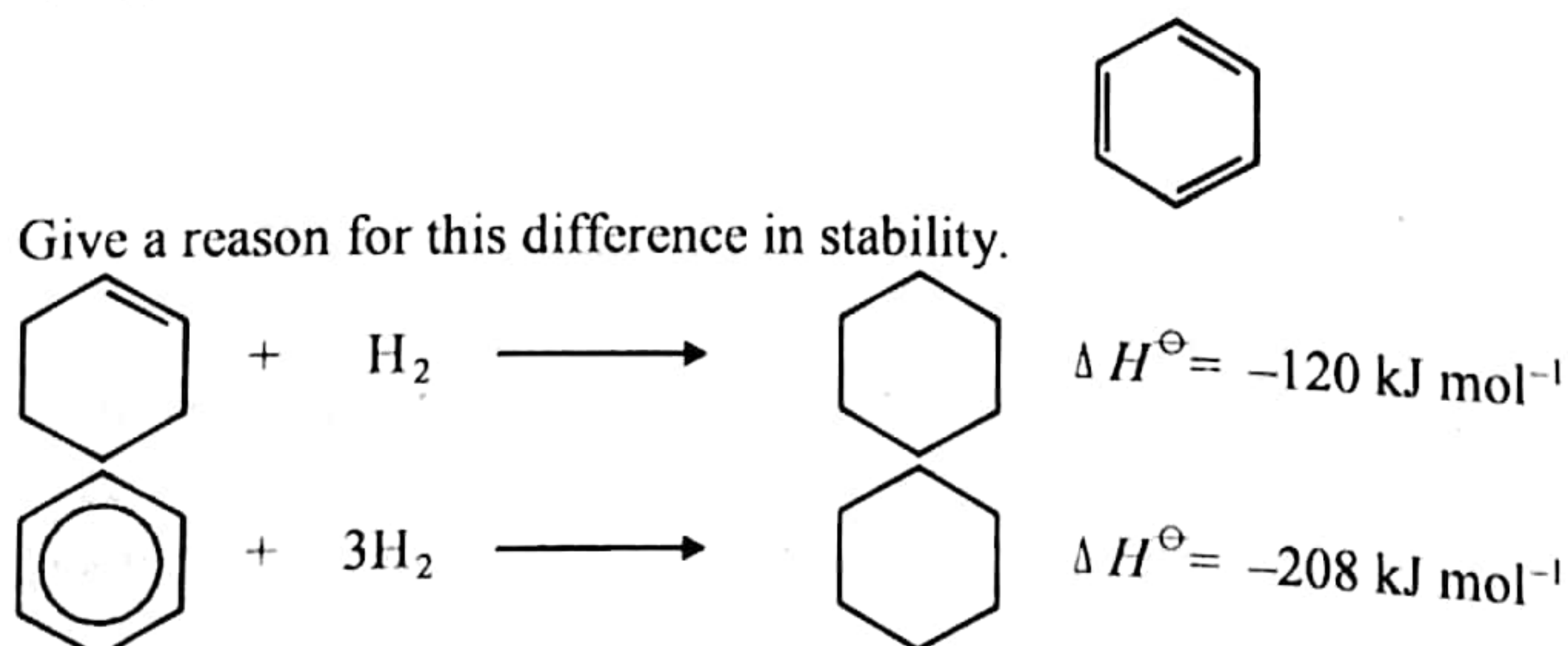
In industry, phenylethene is made from benzene and ethene in a two-step process:



- (i) Give one major use of phenylethene.
- (ii) Identify the reactive species which attacks benzene in Step 1 and write an equation to show how this species is generated.
- (iii) Name the type of reaction which occurs in Step 2.

Question 9

Use the following data to show the stability of benzene relative to the hypothetical cyclohexa-1,3,5-triene.

**Question 10**

Although chlorine is an electron withdrawing group yet it is ortho-para directing in electrophilic aromatic substitution reactions. Why?

Question 11

The usual halogenations of benzene take place only in presence of Lewis acid catalyst like AlCl_3 , whereas phenol (hydroxybenzene) can directly react with bromine? Explain?

Question 12

Phenol is more active towards electrophilic substitution than benzene. Explain?

Question 13

Why it is necessary to use sulphuric acid in nitration of benzene?

Question 14

Highly branched carboxylic acids are less acidic than unbranched acids. Why?

Question 15

In solutions, basic strength of amines is secondary > primary > tertiary. Explain and conclude whether this order is correct or not.

Question 16

Nitration of benzene gives substantial amount of meta product, though $-\text{NH}_2$ is o-p directing group. Explain.

Question 17

(a) The names below are incorrect according to the IUPAC system.

Draw the structural formula for each compound named and give its correct IUPAC name:

i. 2,2 – dimethyl -3-pentene

ii. 2, 2,3- methylbutane

iii. 2-methyl-4-hexene

iv. 3-ethyl-4-methylpentane.

(b) Give the expected product (s) from the reaction of 2-butene with each of the following reagents

i) H^+ , H_2O

ii) H_2 /Catalyst

iii) Cl_2

iv) HOCl

v) O_2 , Flame.

Question 18

Explain why pK_b of NH_3 is 4.75 while that of CH_3NH_2 is 3.34.

Question 19

Compound **E** has molecular formula of C_6H_{10} , bromination of compound **E** yields $\text{C}_6\text{H}_{10}\text{Br}_4$. Treatment of Compound **E** with $\text{Cu}(\text{NH}_3)_2\text{OH}$ solution gives no reaction. Ozonolysis of one mole of Compound **E** yield two moles of CH_3CHO and one mole of $\text{HOC} - \text{CHO}$. Give structural formula of the compound.

Question 20

Three gases which are aliphatic hydrocarbons **A**, **B** and **C** were bubbled through each of the following reagents in turn, liquids bromine, acidified potassium permanganate and ammonical silver nitrate. Compound **A** has no effect in all given reagents. Compound **B** decolourises liquid bromine and potassium permanganate but has no effect on ammonical silver nitrate. Compound **C** decolourises liquid bromine and potassium permanganate and give white precipitate with ammonical silver nitrate solution. When one mole of each gas was bubbled in pure oxygen three moles of CO_2 were produced respectively.

a) Write structural formula of each gas **A**, **B** and **C**

b) Write structure of organic product when,

- i) Gas **B** reacts with KMnO_4
- ii) Gas **B** reacts with bromine
- iii) Gas **C** reacts with bromine
- iv) Gas **C** reacts with ammonical silver nitrate.

c) Write balanced chemical equation for complete combustion of the gases **A**, **B** and **C**.

Question 21

In dichlorination of propane four isomeric product with formula of $\text{C}_3\text{H}_6\text{Cl}_2$ were isolated and designated **A**.....**D**. Each was separated and further chlorinated to give one or more trichloropropanes, $\text{C}_3\text{H}_5\text{Cl}_3$. **A** and **B** give three chloro compounds, **C** give one and **D** give two.

- i) Deduce structures of **C** and **D**
- ii) One of the products of **A** was identical with product from further chlorination of **C**. Suggest structures of **A** and **B**.

Question 22

1.1g of a compound containing C, H and O gives on combustion 1.173g of CO_2 and 0.24g of water. 1.12g of a compound in 25g of water gives a solution freezing at 0.186°C . Calculate the molecular formula of the compound.

Given $K_f = 1.86^\circ\text{C kgmol}^{-1}$

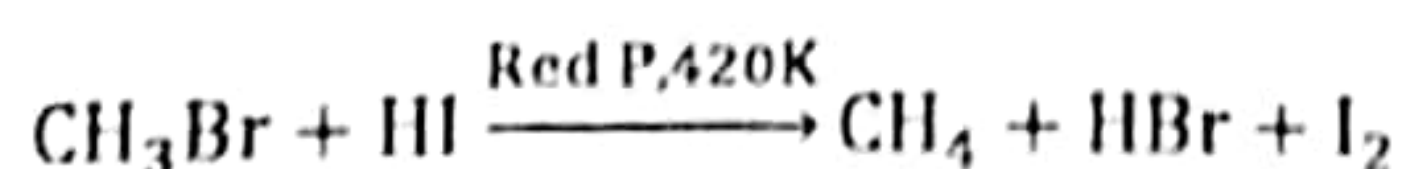
Question 23

Write an equation showing preparations of the following halides from starting material indicated. Show necessary conditions and reagents required for reactions.

- i) $\text{C}_6\text{H}_5\text{CHBrCH}_3$ from $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
- ii) $\text{C}_6\text{H}_5\text{CHBrCH}_2\text{Br}$ from $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (3 reactions are required)
- iii) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$ from $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (3 reactions are required)

Question 24

Hydroiodic acid is powerful reducing agent which reduces haloalkanes to alkanes at **420K** in presence of **red phosphorous**.



- (i) The above reaction is carried out under high pressure, why?
- (ii) What is the use of red phosphorous in the above reaction?

Question 25

Dehydration of an alcohol, $\text{C}_4\text{H}_9\text{OH}$ provides a hydrocarbon **Y**, C_4H_8 . When **Y** is treated with trioxxygen followed by water hydrolysis, only one product is formed which is **Z**.

- a) Write all structural isomers of **Y**
- b) Identify **Y** and **Z**
- c) Write equation for all chemical reactions involved

Question 26

0.64g of CaC_2 reacted with water giving 200cm^3 of C_2H_2 at 27°C and 1 atmosphere. Calculate the percentage purity of calcium carbide in the sample.

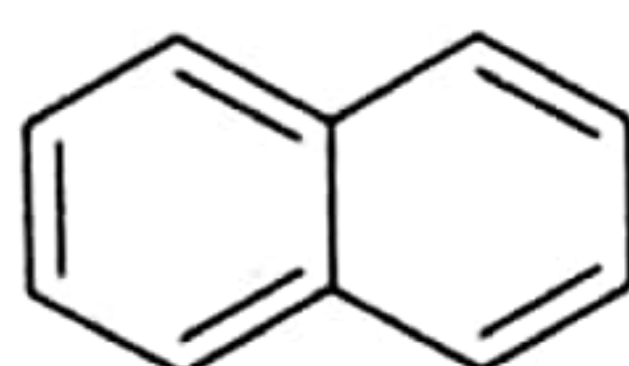
Question 27

A compound is composed of 7.20g of carbon, 1.20g of hydrogen and 9.60g of oxygen. The molar mass of the compound is 180 g/mol. Find the empirical and molecular formulas of this compound.

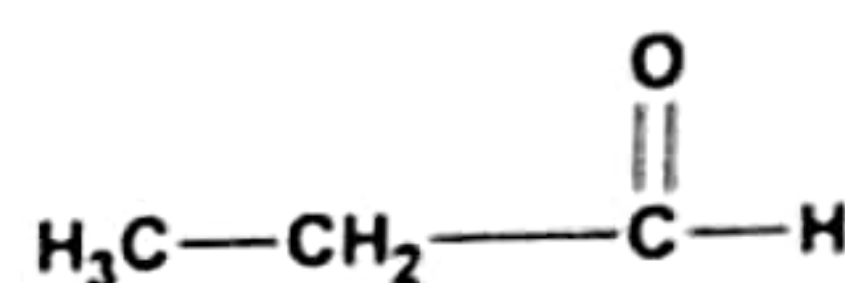
Question 28

Name the type of organic compound each of the following would be classified as:

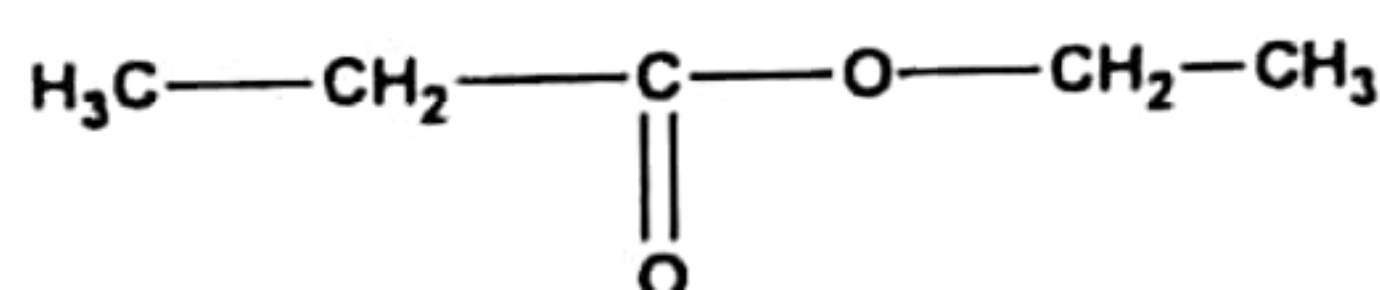
a.



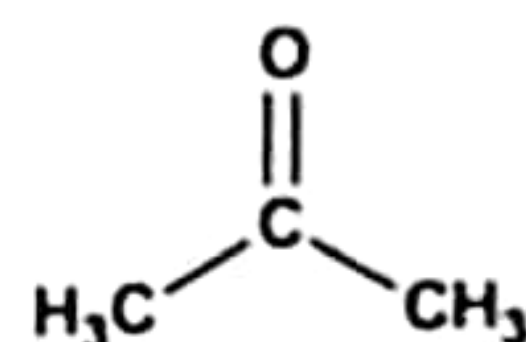
g.



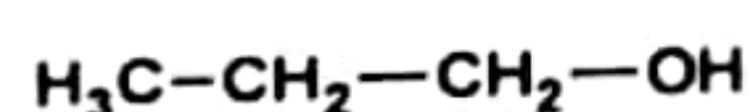
b.



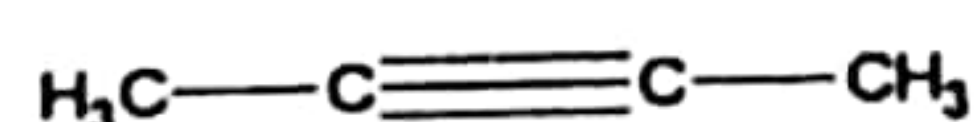
h.



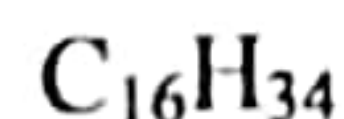
c.



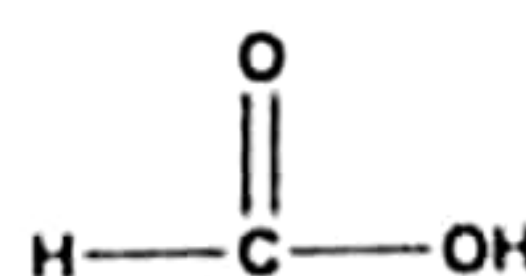
d.



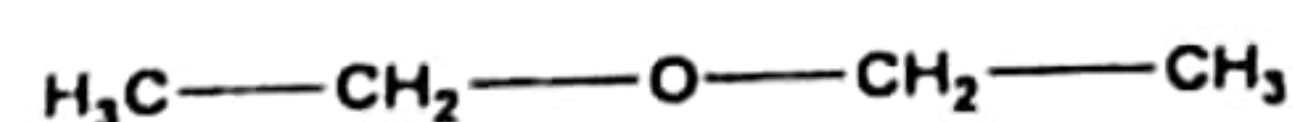
e.



i.



f.



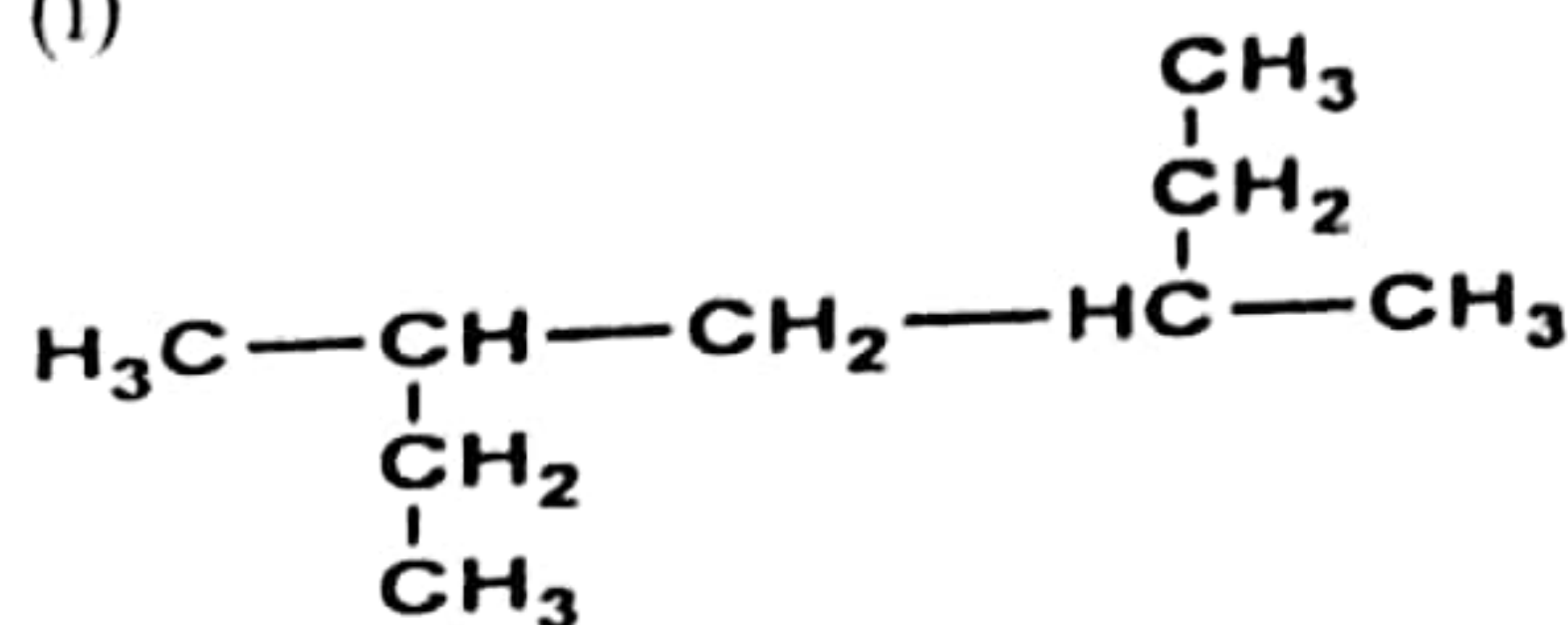
j.



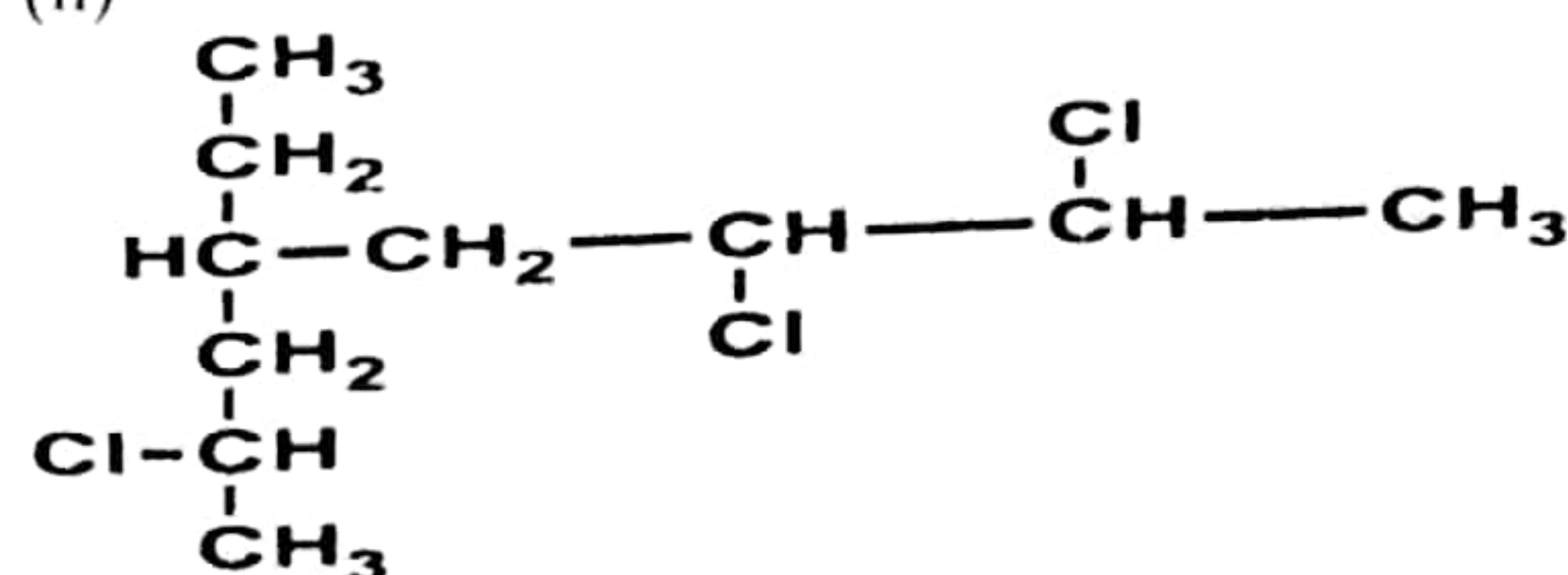
Question 29

Give IUPAC names for the following organic compounds:

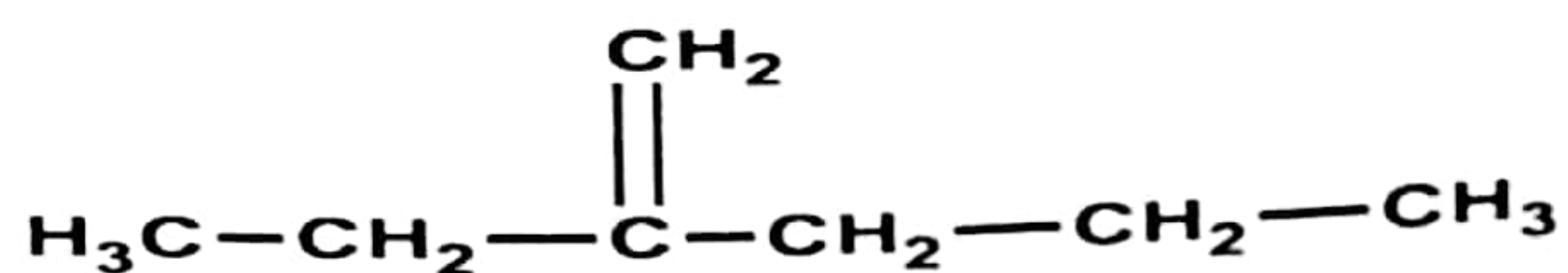
(i)



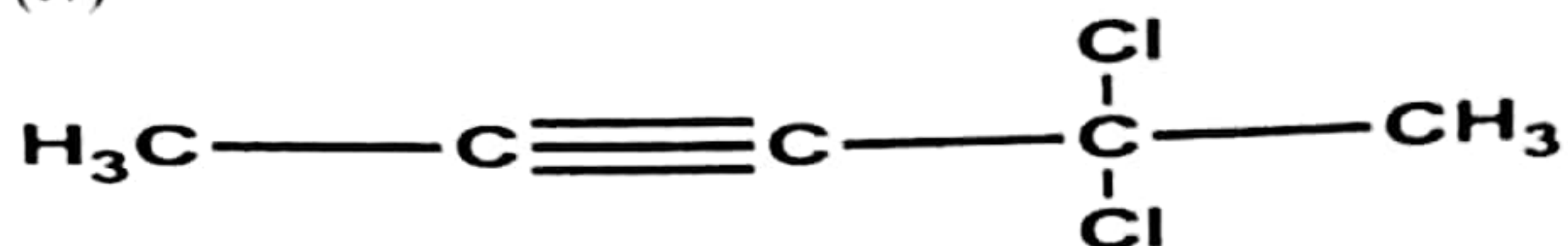
(ii)



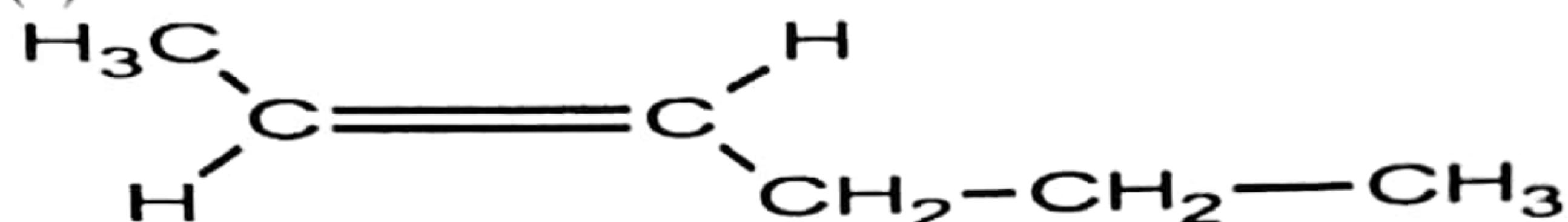
(iii)



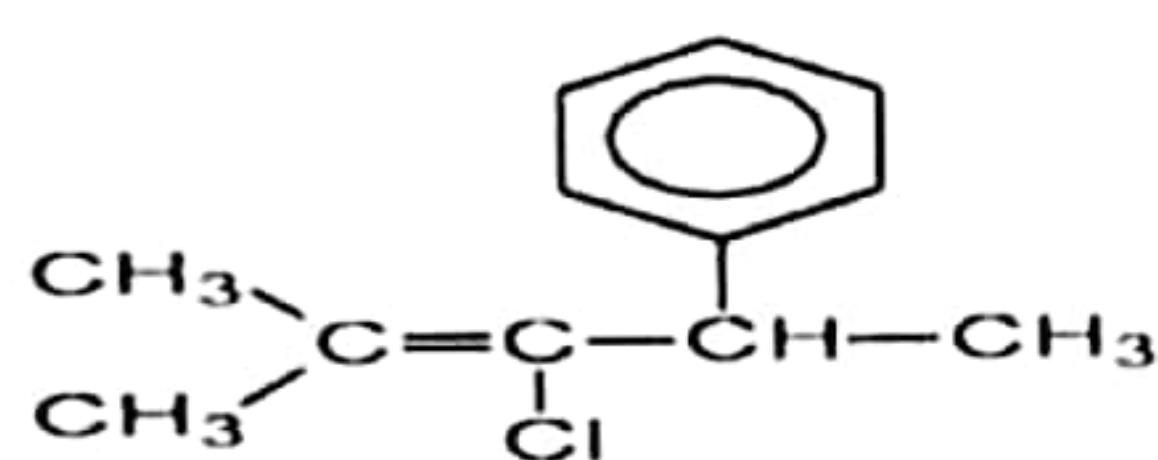
(iv)



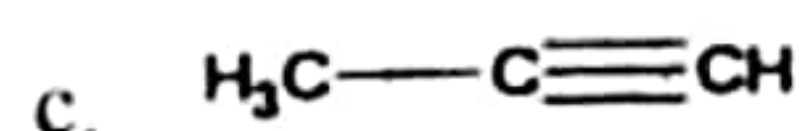
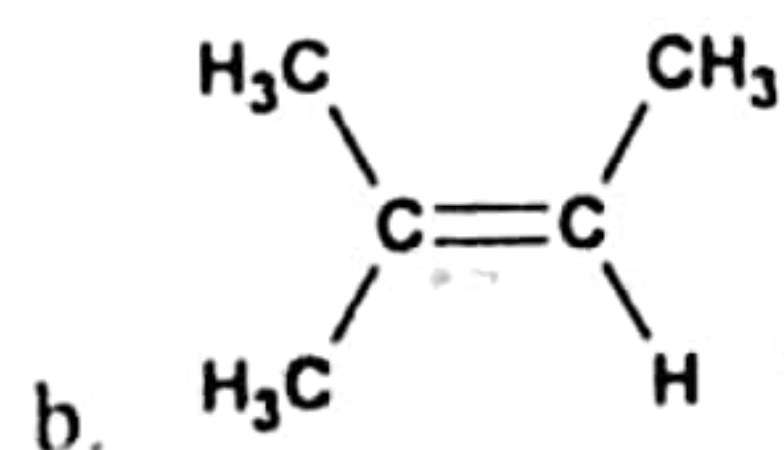
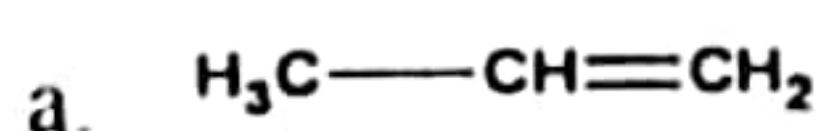
(v)



(vi)

**Question 30**

Predict the product formed when HCl is reacted with each of the following compounds

**Question 31**

Draw and name all of the:

- (a) dibromobenzenes
- (b) dibromochlorobenzenes

Question 32

Give the structures and names of the principal organic products from the reaction of propylbenzene with:

- (a) hydrogen gas, palladium catalyst, mild conditions
- (b) hot potassium permanganate
- (c) nitric and sulphuric acid
- (d) bromine, heat and light
- (e) bromine and aluminum chloride

Question 33

Show how you would prepare the following from benzene and anything else you need:

- (a) 1,2,4-tribromobenzene
- (b) 2,4,6-trinitrobenzene

PART FOUR

CHEMISTRY OF SELECTED

FUNCTIONAL GROUPS

Chapter 17

HALOHYDROCARBONS

Halohydrocarbons are organic compounds which are formed when at least one hydrogen atom of hydrocarbon is replaced by halogen.

They can be:

- Haloalkanes
- Haloalkynes
- Haloalkenes
- Haloarenes

HALOALKANES

These are halohydrocarbons which are formed when at least one hydrogen atom of alkane is replaced by halogen.

- According to number of alkyl groups which are directly bonded to carbon with halogen, haloalkanes can be classified into the following categories:
 - i) Primary (1°) haloalkanes
 - ii) Secondary (2°) haloalkanes
 - iii) Tertiary (3°) haloalkanes.

Primary (1°) haloalkanes

These are haloalkanes whereby a carbon with halogen is directly bonded to one alkyl group only.

- So for haloalkanes with only one halogen the carbon with the halogen is also directly bonded to two hydrogen atoms. That is RCH_2X .

Secondary (2°) haloalkanes

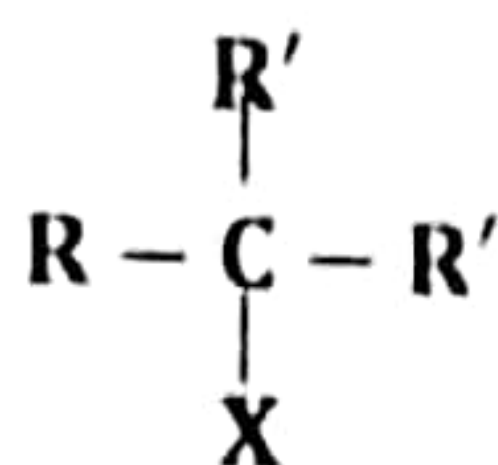
These are haloalkanes whereby a carbon with halogen is directly bonded to two alkyl groups.

- Thus for haloalkane with only one halogen, the carbon with the halogen is also directly bonded to only one hydrogen atom. That is $\text{R} - \text{CHX} - \text{R}'$

Tertiary (3°) haloalkane

These are haloalkanes whereby a carbon containing halogen is directly bonded to three alkyl groups.

- Thus in tertiary haloalkanes there is no hydrogen atom which is directly bonded to carbon with halogen.



NOMENCLATURE OF HALOALKANES

Haloalkanes are named by naming halogen as substituent of alkane.

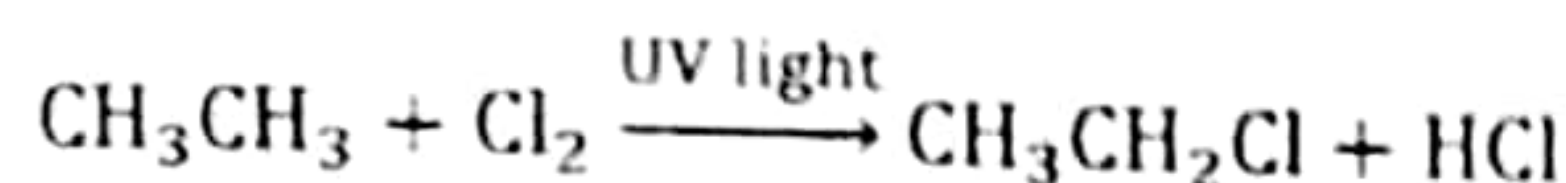
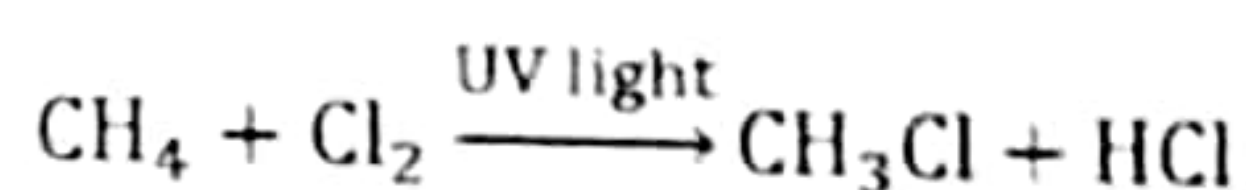
- There is no special preference given to halogen, for example,

$$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \underset{\text{Cl}}{\text{CH}}\text{CH}_2\text{CH}_3$$
 is named as 4-chloro-2-methylhexane

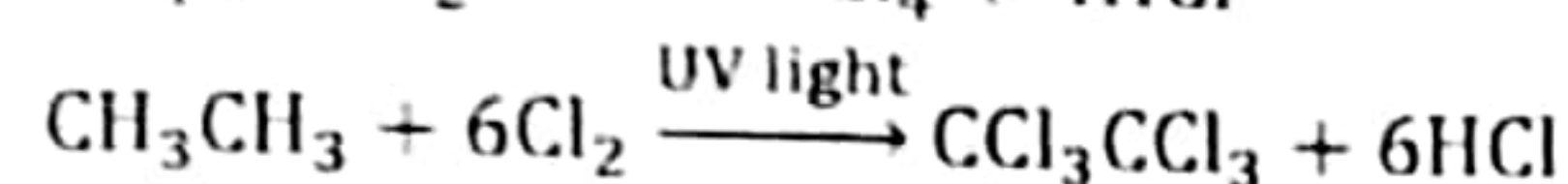
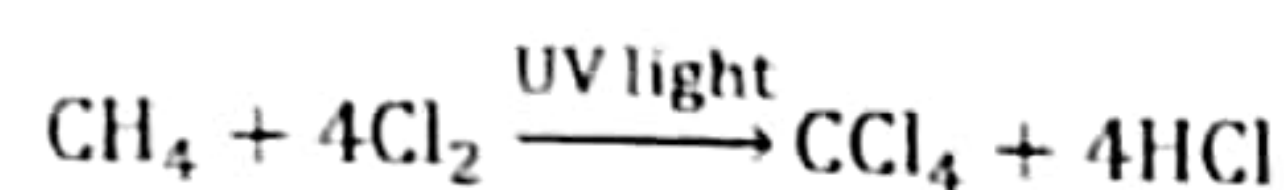
PREPARATIONS OF HALOALKANES

Free radical substitution reaction of alkanes

Alkane undergoes free radical substitution reaction to give haloalkane.

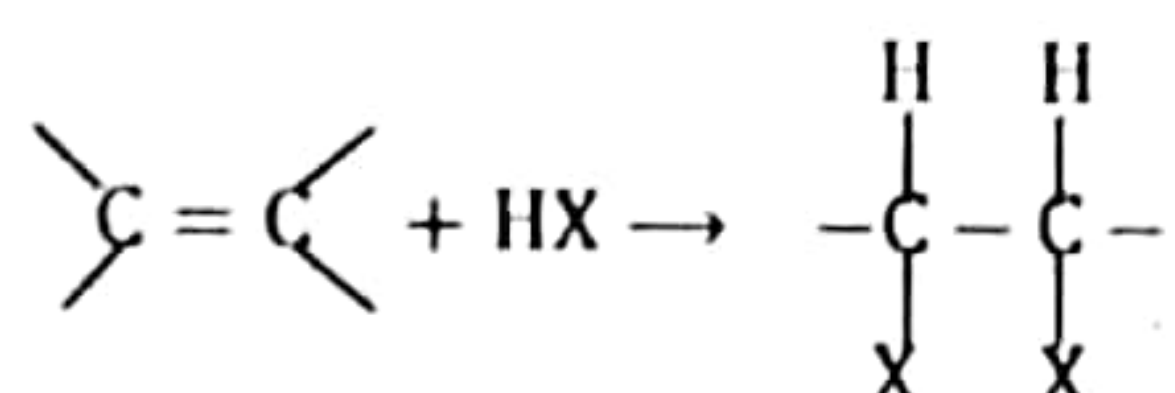


In the above reactions, chlorine must be present in limited amount so as to prevent further chlorination of the product otherwise:



However this method (direct halogenation) is not good preparation method as the halogen may attack any carbon atom of the hydrocarbon. Therefore, the product is a mixture of several haloalkanes whose separation is difficult because they all have more or less the same boiling point. But haloalkanes are used as industrial solvent and therefore the mixture obtained by halogenations can be used as such.

Halohydrogenation of alkenes



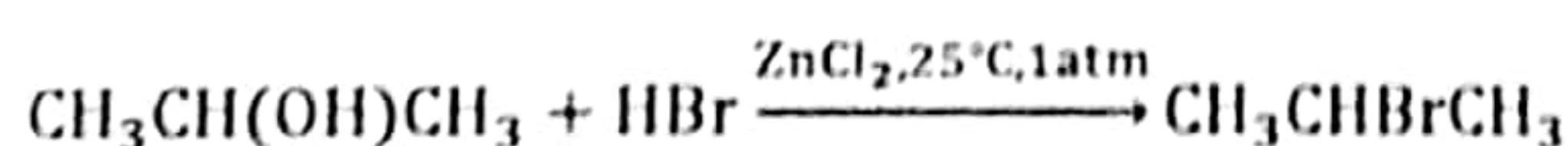
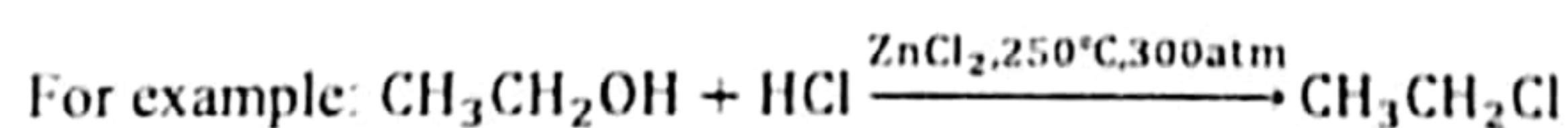
Examples:



Halogenation of alcohol

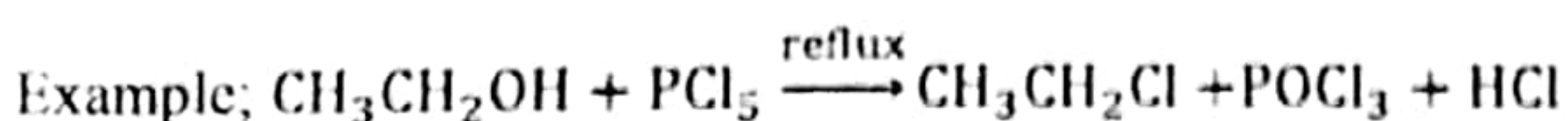
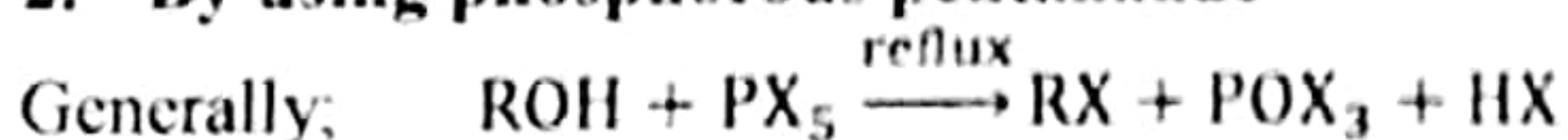
1. By using hydrogen halide

Alcohol reacts with hydrogen halide to give haloalkane.

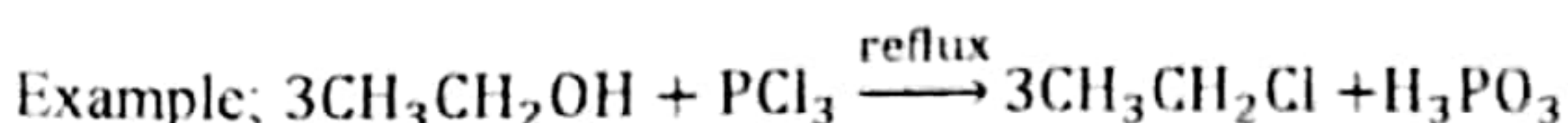
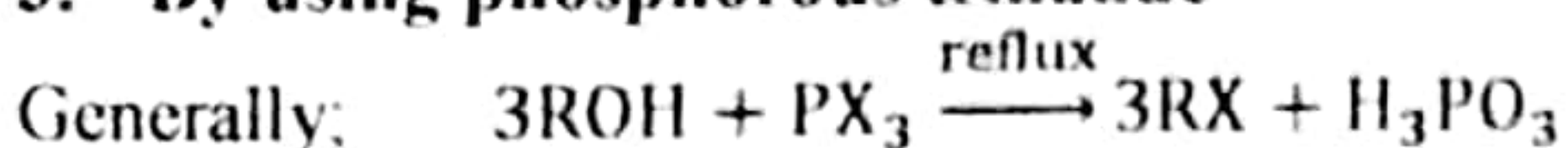


Preparation of haloalkane by this method is going to be discussed in detail in the chemical reactions of alcohol.

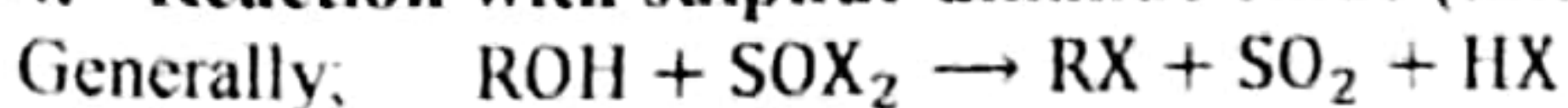
2. By using phosphorous pentahalide

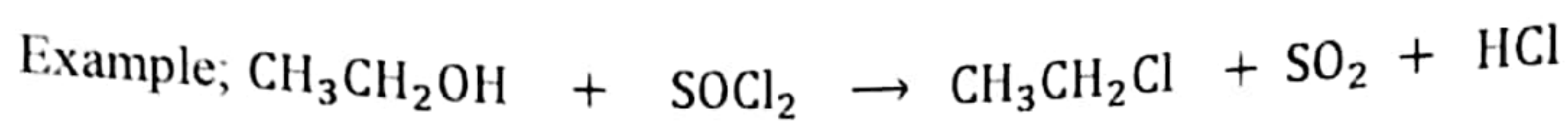


3. By using phosphorous trihalide



4. Reaction with sulphur dihalide oxide (thionyl halide)





Thionyl chloride

The reader should understand that:

Among the above method for preparation of haloalkane by halogenations of alcohol the reaction which employ SOCl_2 is more efficient why?

- This is simply because all byproducts SO_2, HCl , are gases and therefore escape easily from the container thus eliminating any possibility of reverse reaction.

PHYSICAL PROPERTIES OF HALOALKANES

- Melting and boiling points of haloalkanes are greater than those of corresponding members of alkanes (alkanes whose molecular mass do not differ much with those of haloalkanes) as result of high polarity of $\text{C} - \text{X}$ bond ($\text{C}^{\delta+} - \text{X}^{\delta-}$).
- Haloalkanes are soluble in organic solvent (Haloalkane themselves are good organic solvents).
- They tend to form miscible mixture with another organic solvent but are almost insoluble in water.
- However compared to alkane, haloalkane are slightly more soluble in water due to polarity of $\text{C} - \text{X}$ bond.

CHEMICAL REACTIONS OF HALOALKANES

Haloalkanes undergo the following chemical reactions:

- Elimination reactions
- Nucleophilic substitution reactions
- Reaction which lead to formations of Grignard reagent
- Wurtz reactions and
- Reduction

Elimination reactions

Elimination and nucleophilic substitution reactions in haloalkanes are competitive reactions.

Condition which favour elimination reactions are:

- (i) The reaction should be undertaken in **presence of non aqueous medium**.
(in this case the reaction is undertaken in presence of alcohol)

Note: More polar solvent like water makes carbon with halogen more positive polarised and therefore favouring more nucleophilic substitution reaction.

- (ii) The reaction should be undertaken in **presence of strong and concentrated base like concentrated KOH**.
- (iii) The reaction should be undertaken **at high temperature**.
- (iv) **If the haloalkane is tertiary**.

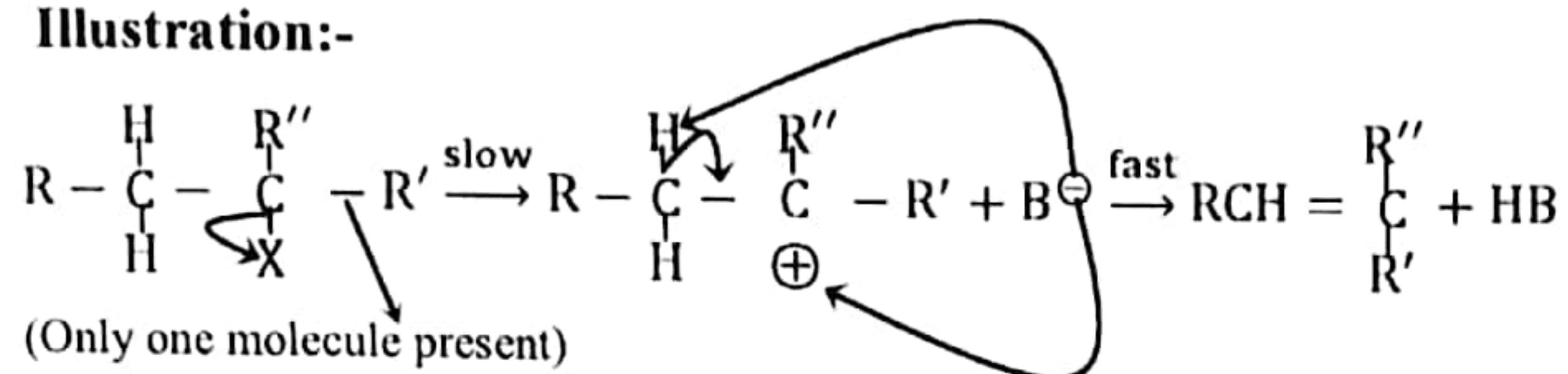
There are two types of mechanism of elimination reaction in haloalkane namely:

- (b) E1 mechanism
- (c) E2 mechanism

E1 mechanism

This is the mechanism of elimination reaction whereby there is only one molecule which is involved in the rate determining step. In simple words, its rate determining step is **unimolecular**. Where, rate determining step is the slowest step in the reaction mechanism.

- E1 mechanism is more common in tertiary haloalkane as result of high stability of intermediate carbenium ion which is brought about by very strong positive inductive effect exerted by three alkyl groups from three directions.

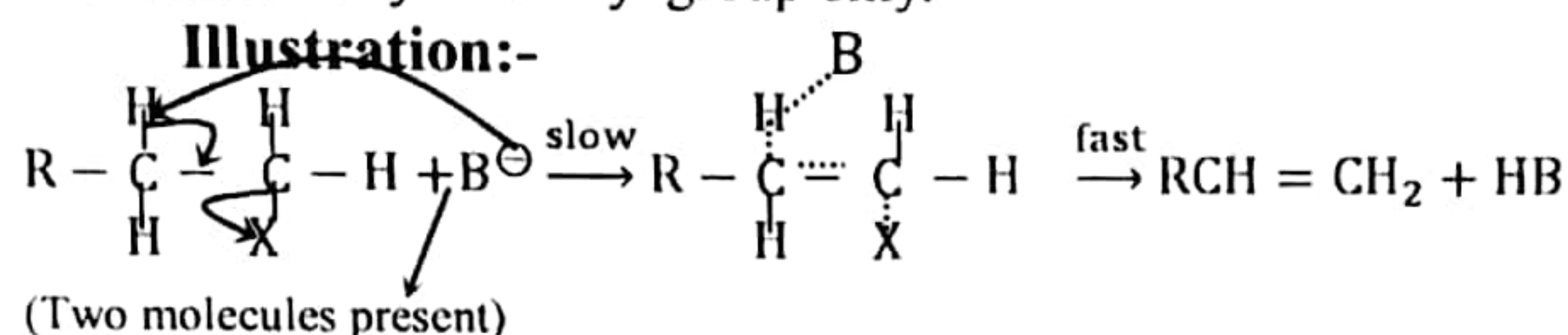
Illustration:-

Where B^- is lewis base (nucleophile).

E2 mechanism

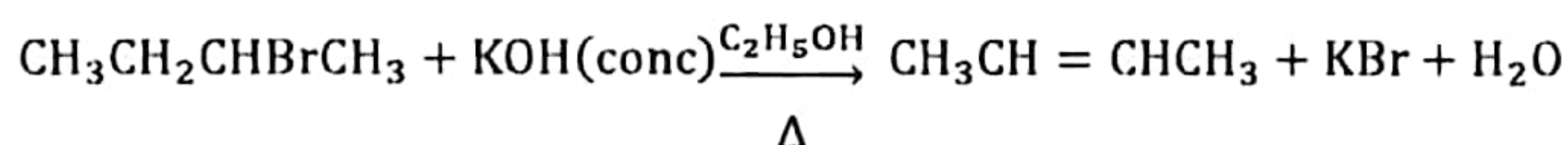
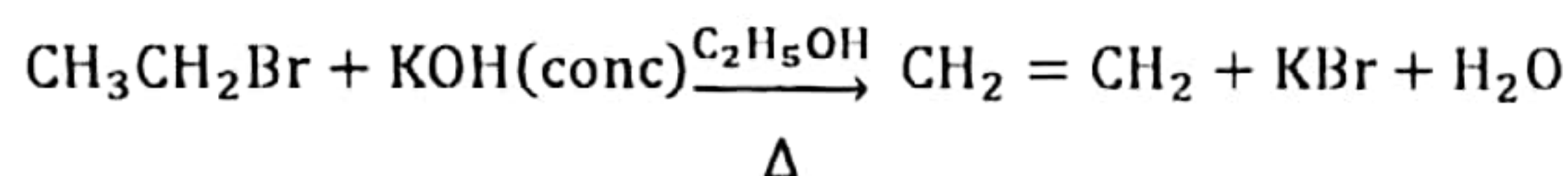
This is the *elimination reaction mechanism* whereby there are two molecules which are involved in the rate determining step.

E2 mechanism is more common in primary haloalkane due to unstability of intermediate carbenium ion which would be formed if it would undergo E1 mechanism as result of weak positive inductive effect exerted by one alkyl group only.

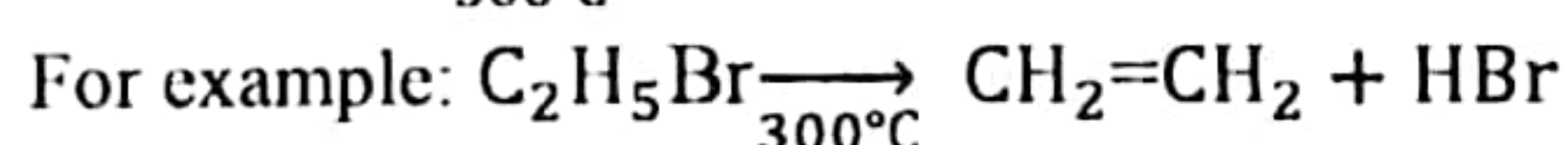
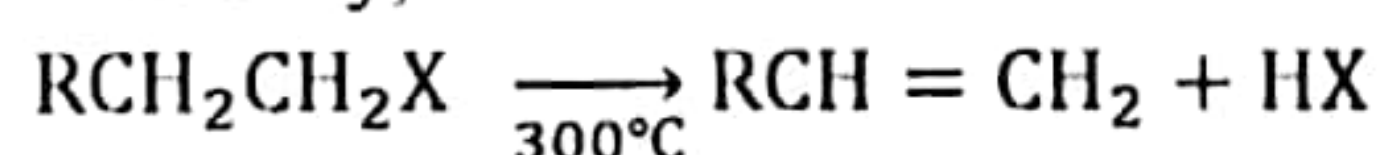


Where B^- is lewis base (nucleophile).

Example of elimination reactions in haloalkanes are:



Elimination of haloalkane to alkene can also be done by just heating the haloalkane to 300°C
Generally;



Possibility of haloalkanes to undergo elimination reactions follows the following trend:

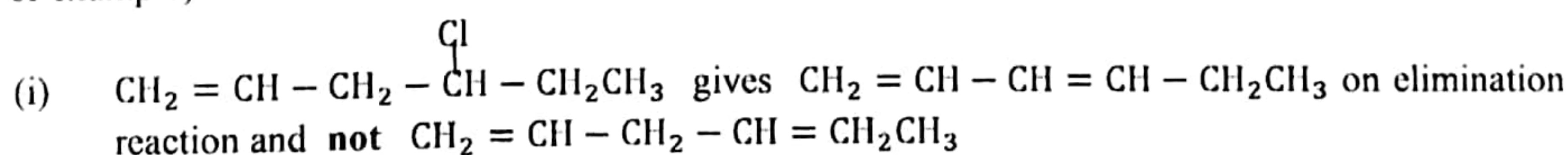
Tertiary haloalkanes > Secondary haloalkanes > Primary haloalkanes

The reader should understand that:

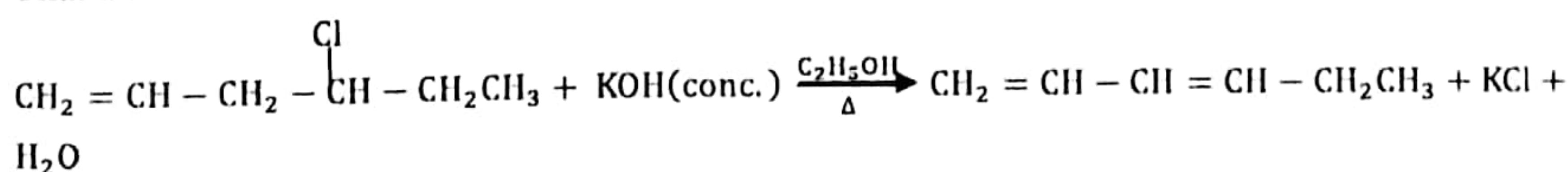
Conjugated double bond alkene is more stable than other forms of alkene (cumulated and isolated double bond alkene). This is because pi (π) bond in conjugated alkene are stabilised by mesomerism (Remember that conjugate state favour occurrence of mesomerism in the organic compound).

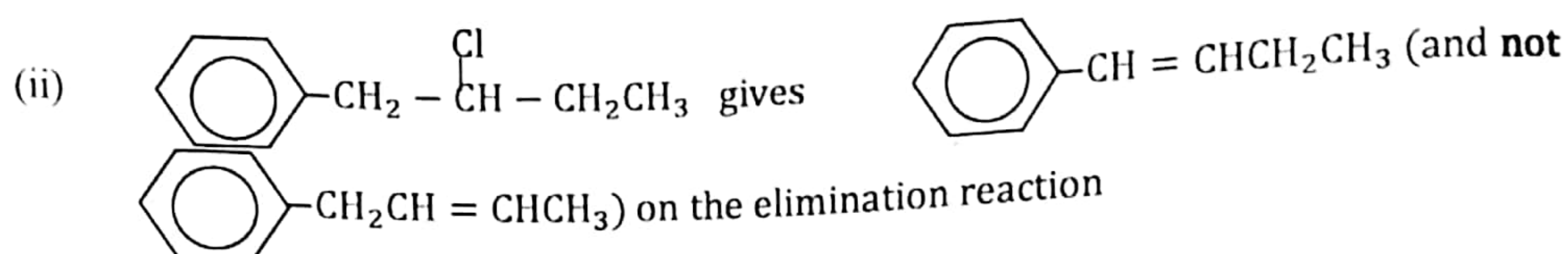
- So when there is a possibility of forming more than one type of diene (or any alkene with more than one $\text{C} = \text{C}$), the diene (alkene) with conjugated double bond becomes the major product.

For example;

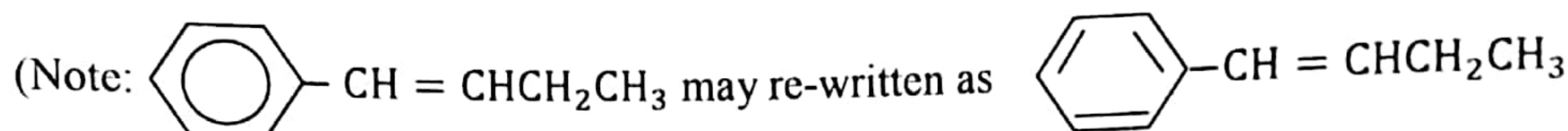
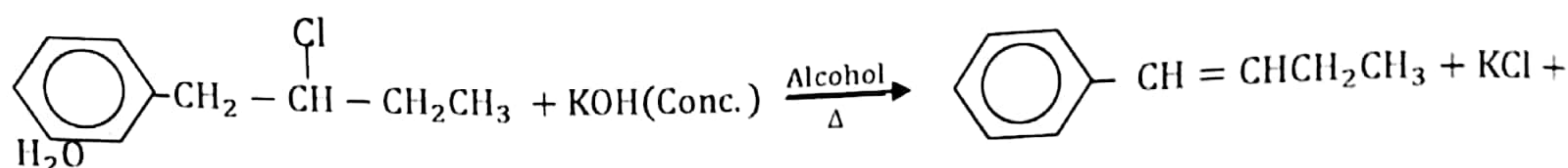


That is:





That is;



Where the second formula shows clearly the presence of conjugated double bond in the compound)

Nucleophilic substitution reactions

Most of chemical reactions in haloalkane are nucleophilic substitution reaction. Nucleophilic substitution reactions in haloalkane undergo in two type mechanism namely;

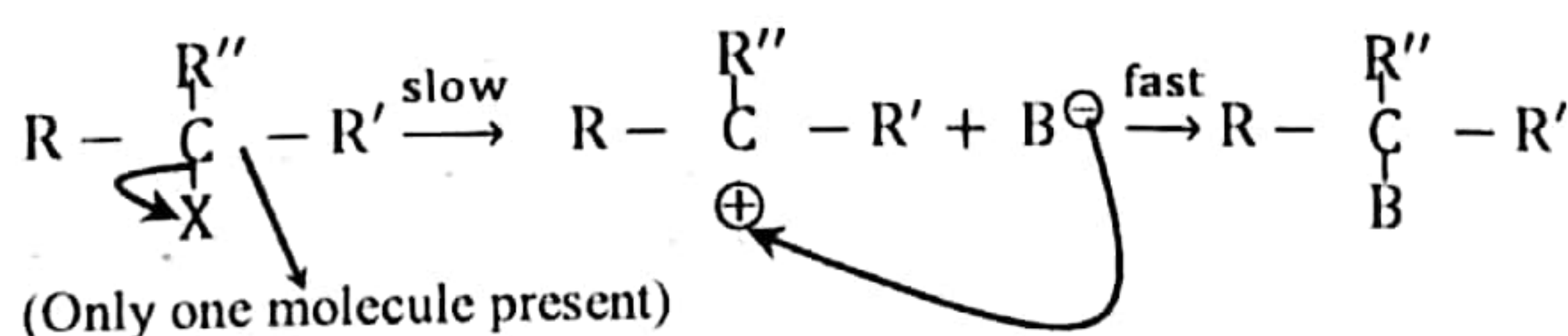
- S_N1 mechanism and
- S_N2 mechanism

S_N1 Mechanism

S_N1 mechanism is the nucleophilic substitution reaction mechanism whereby there is only one molecule which is involved in the **rate determining step**. In other words; rate determining step of S_N1 mechanism is **unimolecular**.

S_N1 mechanism is more common in tertiary haloalkane as a result of high stability of intermediate carbenium ion which is brought about by strong positive inductive effect exerted by three alkyl groups.

Illustration:-

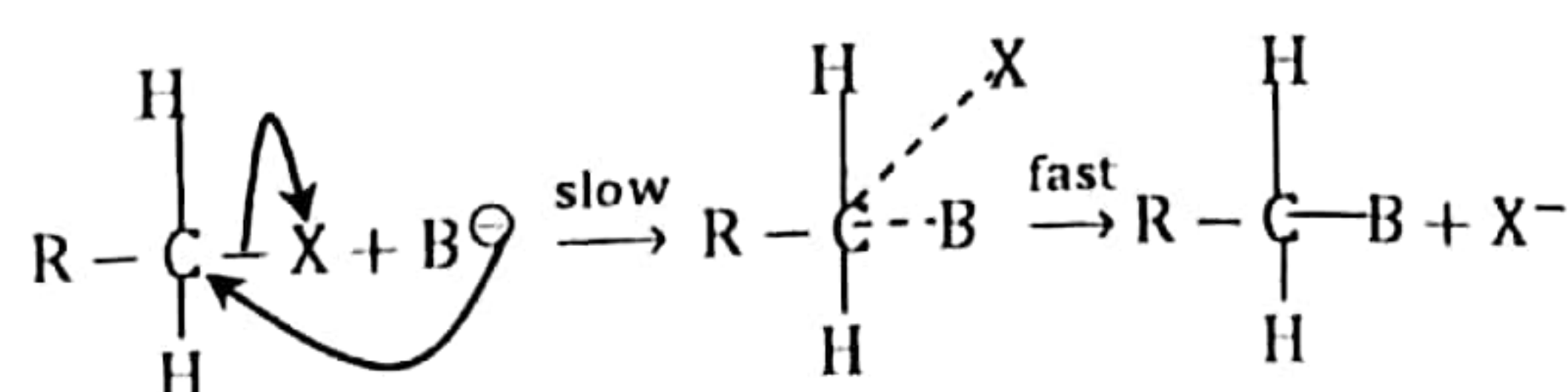


Where B^- is lewis base (nucleophile).

S_N2 mechanism

S_N2 mechanism is the nucleophilic substitution reaction mechanism whereby there are two molecules in the rate determining step. In other words; rate determining step of S_N2 mechanism is **bimolecular**.

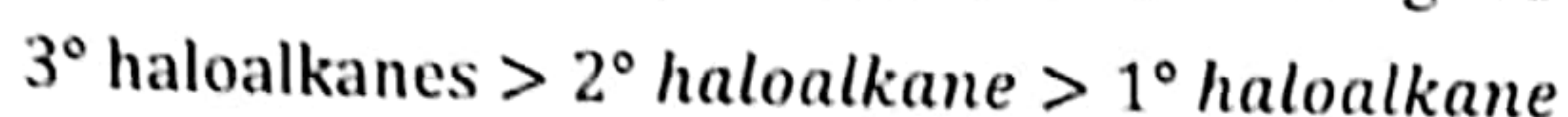
- It is more common in primary haloalkanes (also in secondary haloalkanes) where if they would undergo S_N1 mechanism they would form unstable intermediate carbenium ion.



(Two molecules present)

Where B^- is lewis base (nucleophile).

Generally reactivity of haloalkanes towards nucleophile follows the following order:



↓
Decrease in ability of undergoing nucleophilic substitution reaction

Factors favouring S_N1 and S_N2 mechanism

The substitution reaction will undergo either S_N1 mechanism or S_N2 mechanism depending on the following factors;

Nature of haloalkane

- Primary haloalkanes undergo S_N2 mechanism while tertiary haloalkanes undergoes S_N1 mechanism. Secondary haloalkanes react through both S_N1 and S_N2 mechanism.

Nature of nucleophile

- Strong nucleophiles favours S_N2 mechanism while weak nucleophiles favours S_N1 mechanism.

Concentration of nucleophile

- High concentration of nucleophiles favours S_N2 mechanism while low concentration of nucleophile favours S_N1 mechanism.

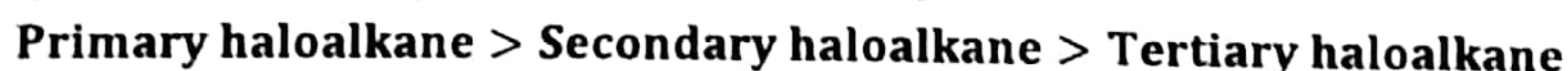
Nature of solvent

- A polar solvent favours S_N1 mechanism as they cause ionisation of haloalkane and therefore it activates the formation of carbenium ion while non-polar solvent (or solvent of low polarity) favours S_N2 mechanism.

Four important points to note!

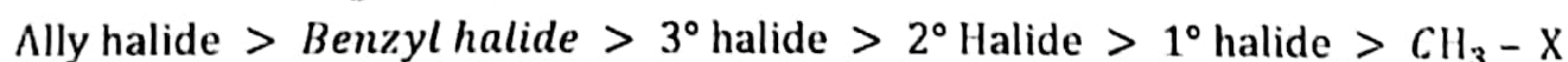
- Since the rate determining step of S_N1 reaction is unimolecular, the reaction rate depends only upon the concentration of haloalkane and hence is of the first order. That is

$$R = K [\text{Haloalkane}]$$
- So unlike in the S_N1 reaction where the rate of reaction depends upon the concentration of haloalkane only, in S_N2 reaction, the rate of reaction depends upon the concentration of both the haloalkane and the Lewis base (Nucleophile). That is $R = K[\text{Haloalkane}][B^-]$
- The ability of haloalkane to undergo S_N1 mechanism depends in the stability of the intermediate carbenium ion.
- Since 3° carbenium is most stable, the order of reactivity for S_N1 reaction becomes
Tertiary haloalkane > Secondary haloalkane > Primary haloalkane
- The ability of haloalkane to undergo S_N2 mechanism depends on the steric hindrance experienced by carbon with halogen in the haloalkane.
- Since the carbon with halogen in tertiary haloalkane experience strongest steric hindrance, the order of reactivity of reactivity for S_N2 mechanism becomes;



Don't get tired, here is another important point!

The reactivity of different classes of haloalkane in nucleophilic substitution reaction of S_N1 mechanism is of the following order;



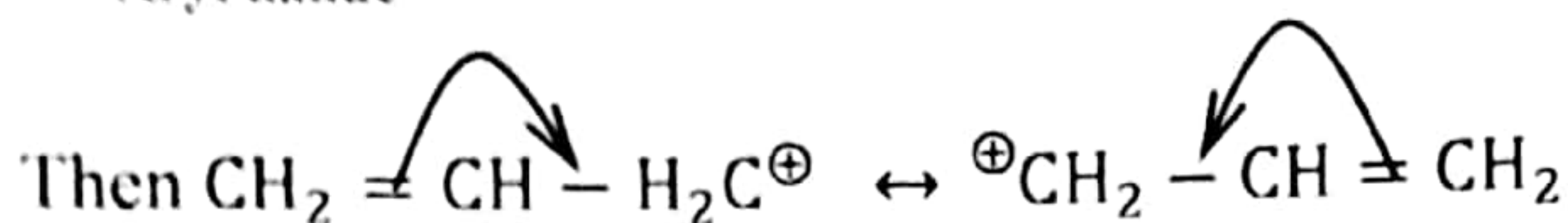
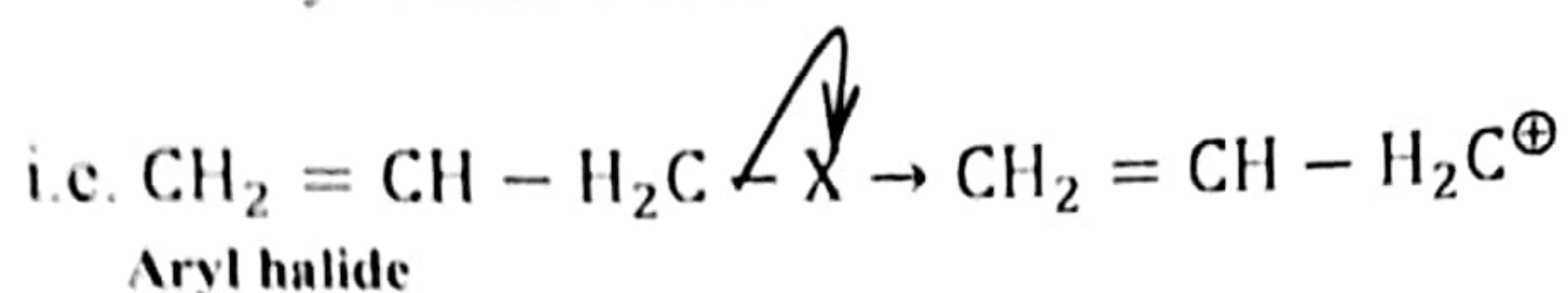
Most reactive

least reactive

Reason for the order of reactivity

The reactivity depends upon the stability of the intermediate carbenium ion. Greater the stability of the carbenium ion, greater is the reactivity in the nucleophilic substitution.

- ❖ Allyl carbenium ion is stabilised through mesomerism (resonance) and is the most stable. Therefore Allyl halide is more reactive.



(Resonance structure of carbenium ion formed on aryl after heterolytic bond cleavage of C - X bond)

- ❖ Phenyl group in benzyl halide is better electron realizing group than alkyl groups due to its nucleophilic character. Therefore the intermediate carbenium ion in the reaction of benzyl halide is more stable and hence the halide becomes more reactive than the alkyl halides.
- ❖ Alkyl groups release electrons towards the intermediate carbenium ion thus stabilizing the ion through positive inductive effect. Greater positive inductive effect, greater the stability of carbenium ion and hence the reactivity of corresponding haloalkane (alkyl halide) will be higher.
 - Tertiary (3°) haloalkane exerts greatest positive inductive effect because three alkyl groups are attached to the carbon with halogen.
 - Secondary (2°) haloalkane has two alkyl groups and the positive inductive is less than in tertiary haloalkane.
 - Primary (1°) haloalkane has one alkyl groups and therefore the positive inductive effect in it is far less than secondary and tertiary haloalkane.
 - In $\text{CH}_3 - \text{X}$, there is no alkyl group attached to carbon with halogen and hence there is no +I at all.

And here is the last point to study before looking to examples of nucleophilic substitution reactions in haloalkanes!

The reactivity of primary haloalkane towards nucleophilic substitution reaction is according to the following order:



Most reactive

Least reactive

Reasons for the order of reactivity

Iodine is good leaving group because:

- C - I bond is weaker
- Iodine is least electronegative of all halogens
- Iodine has the largest size of all halogens and therefore C - I bond length is largest and hence its bond energy is lowest
- Iodine is solvated to a less extent because of its small charge density and large size.

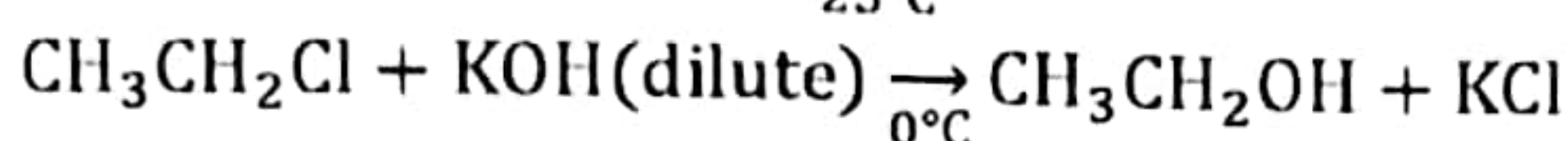
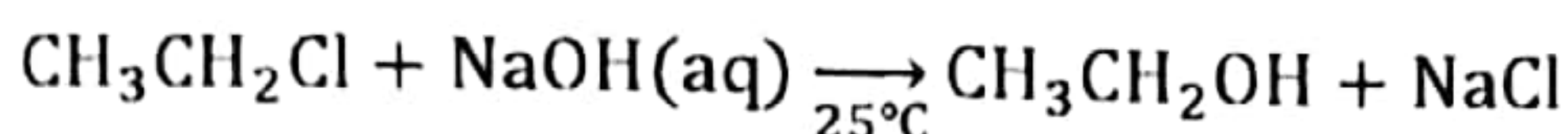
The above three characters decrease regularly as you descend the halogen group.

Examples of nucleophilic substitution reactions of haloalkanes

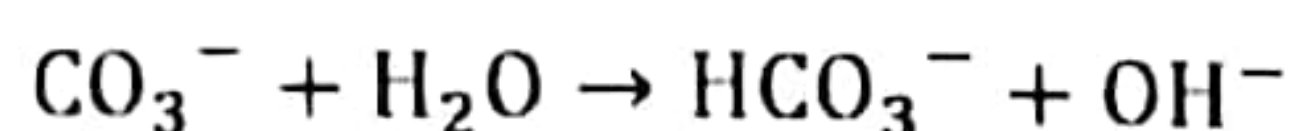
1. Formation of alcohol

Haloalkanes react with alkaline solution like NaOH (aq) yielding alcohol.

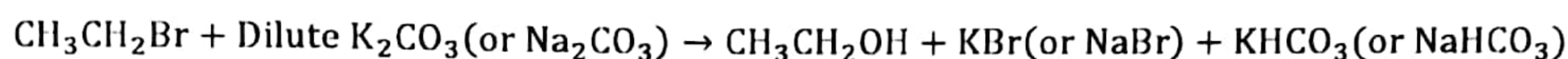
Examples:



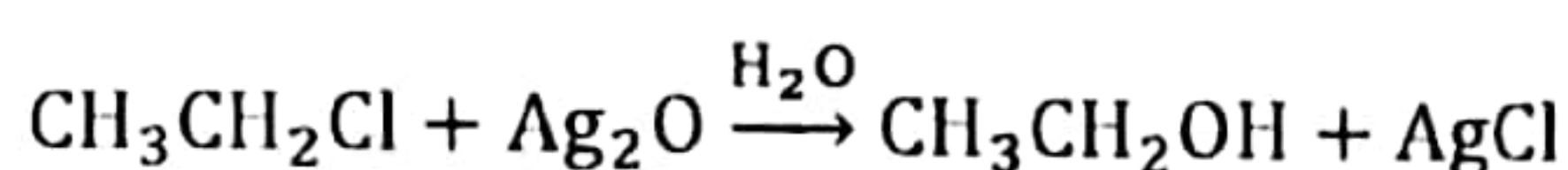
Solution of carbonate may be used instead of hydroxide as the source of OH^-



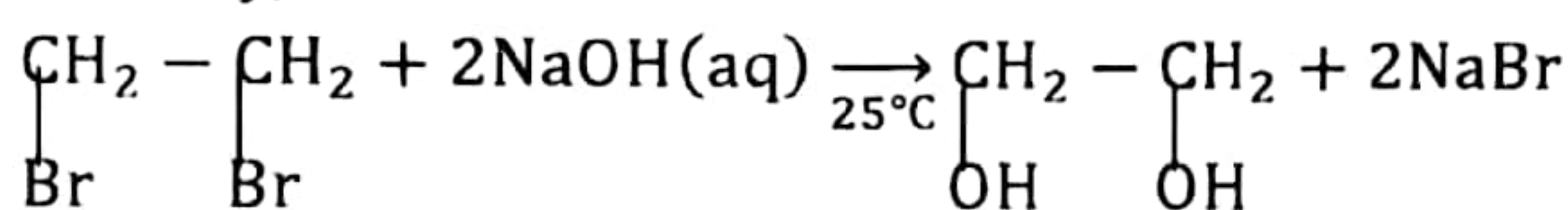
For example;



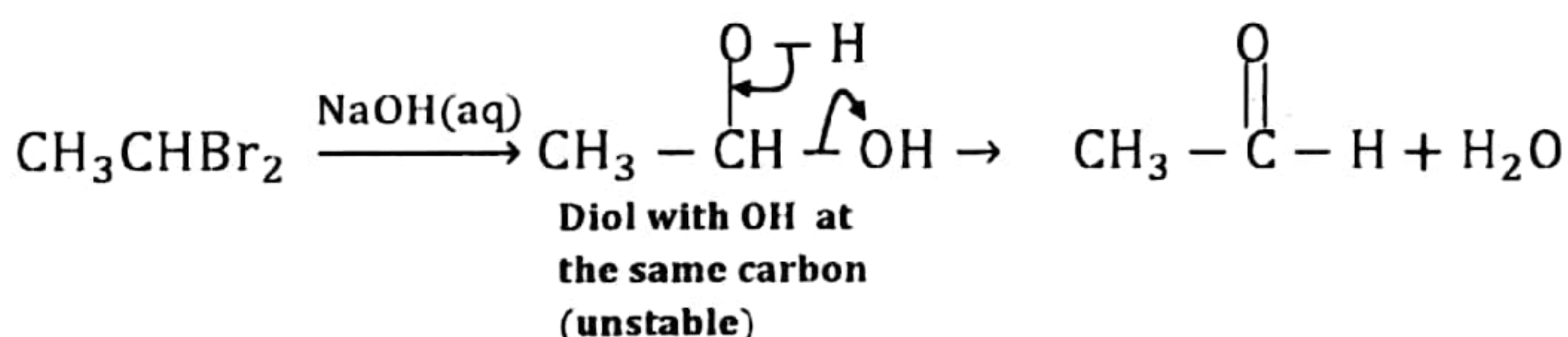
To avoid formation of elimination product, moist silver oxide can be used.



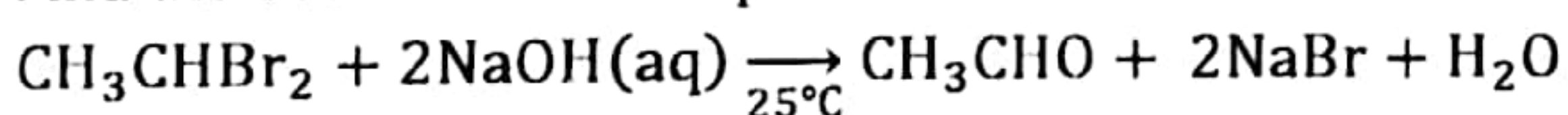
Similarly;



But;

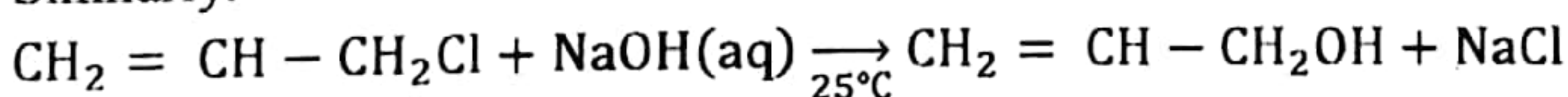


And the overall reaction equation becomes:



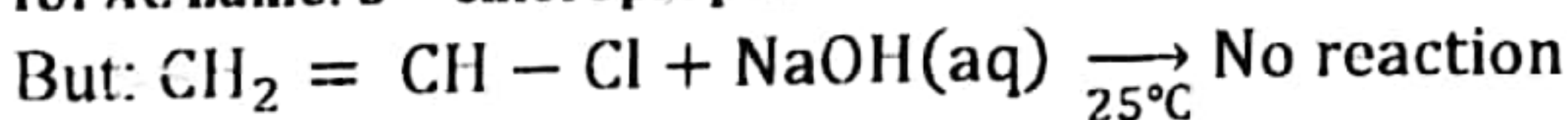
Also;

Similarly:



Common name: allyl Chloride

IUPAC name: 3-chloropropene

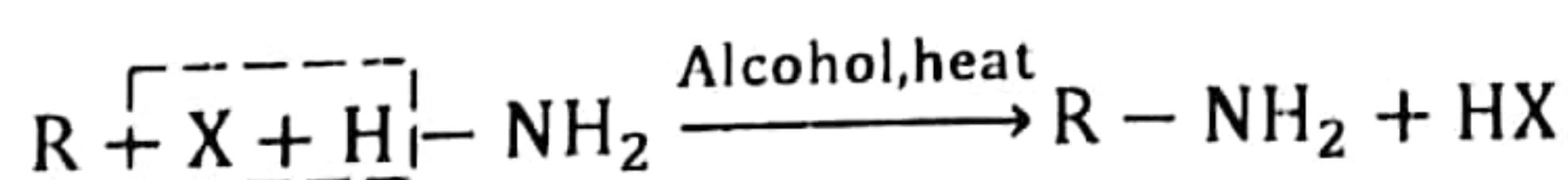


This is because in vinyl chloride ($\text{CH}_2 = \text{CH} - \text{Cl}$), there is high electron density of $\text{C} = \text{C}$ in the carbon with Cl which repel incoming OH^- (nucleophile) unlike in allyl chloride where C with $\text{C} = \text{C}$ has no chlorine atom.

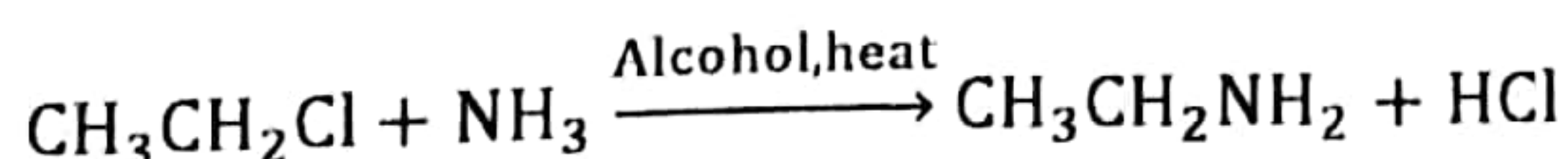
2. Formation of amines

When haloalkane is heated with ammonia, amine is formed.

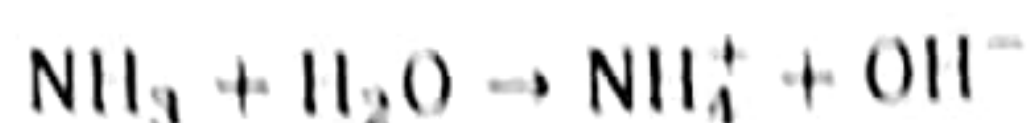
Generally;



Example;



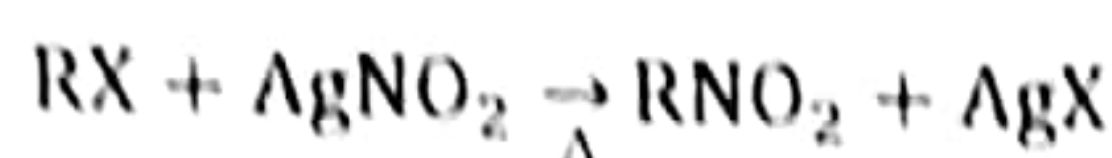
The reaction between haloalkane and the ammonia must take place in alcoholic medium and not aqueous medium because under aqueous medium the ammonia would react with water to give hydroxyl ion (OH^-) which may react with haloalkane to give alcohol.



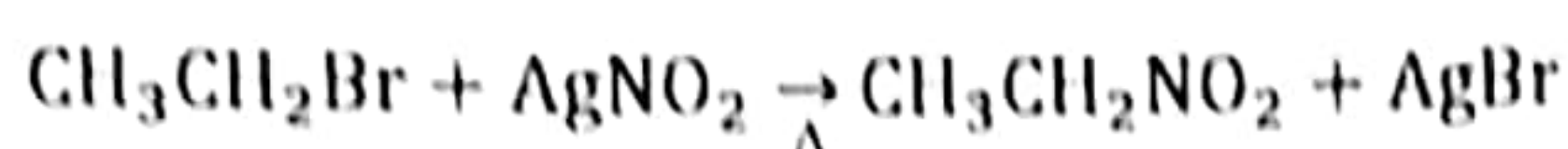
3. Formation of nitroalkanes

When haloalkane is heated with silver nitrite, nitroalkane is formed.

Generally;



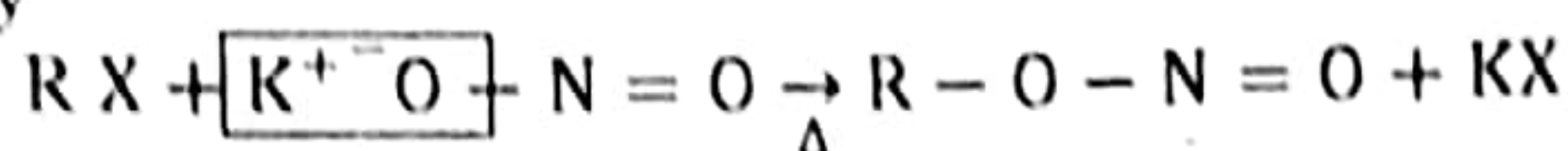
Examples:



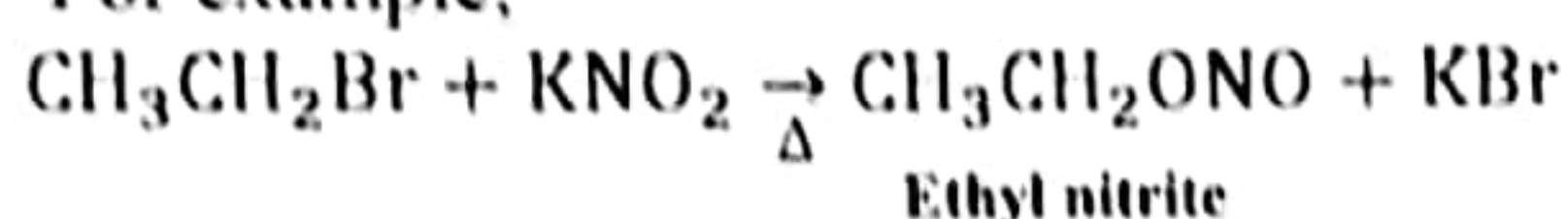
But;

With sodium or potassium nitrite, haloalkane forms alkyl nitrites.

Generally

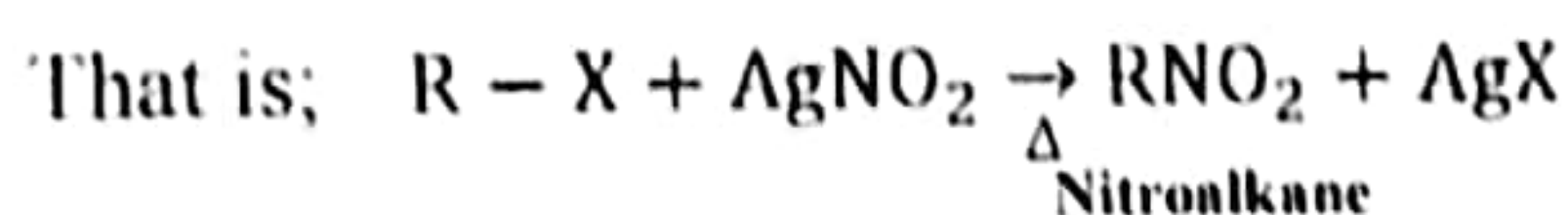


For example;



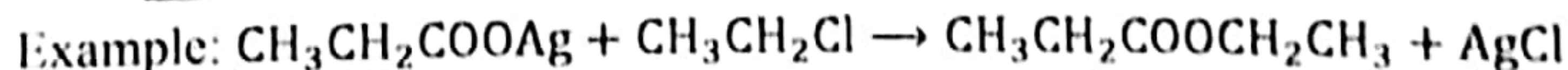
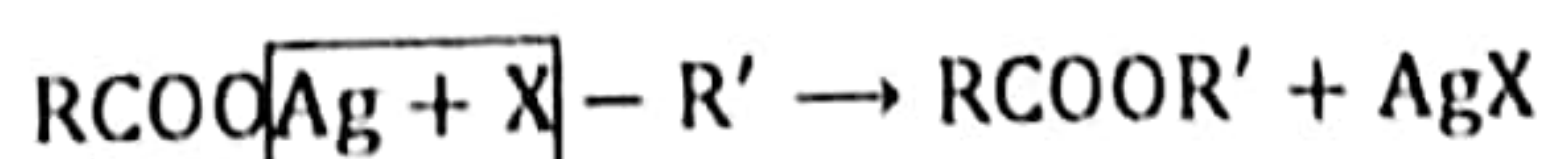
Be careful!

In the above reaction, the bond between $\text{K} - \text{O}$ in KNO_2 (Potassium nitrite is ionic and therefore the negative charge on oxygen is attacking site and hence alkyl nitrite ($\text{R} - \text{O} - \text{N} = \text{O}$) is formed. But if the nitrite is covalent like in AgNO_2 where the bond between $\text{Ag} - \text{O}$ is covalent, the nucleophilic attacking site becomes lone pair on nitrogen and nitroalkane is formed.



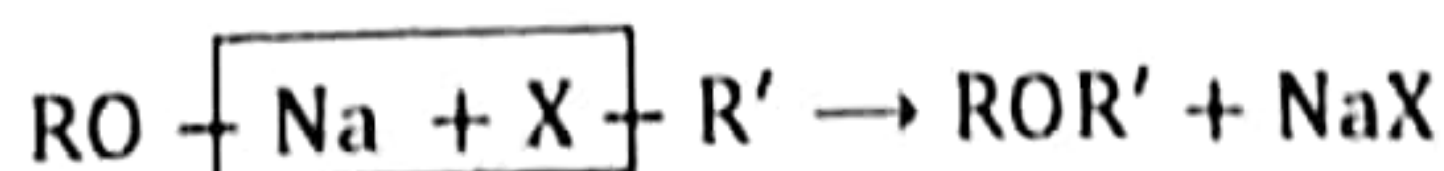
4. Formation of ester

Generally



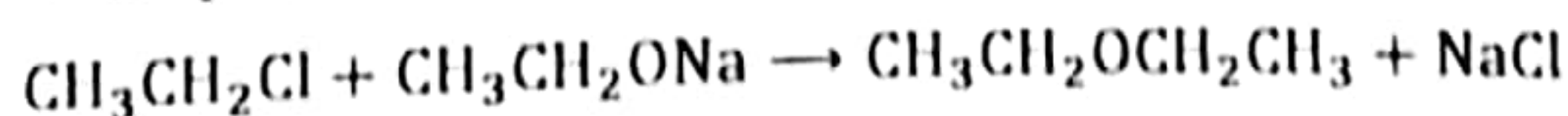
5. Formation of ether (Williamson's synthesis)

Generally;



Sodium alkoxide

Example;



Sodium ethoxide

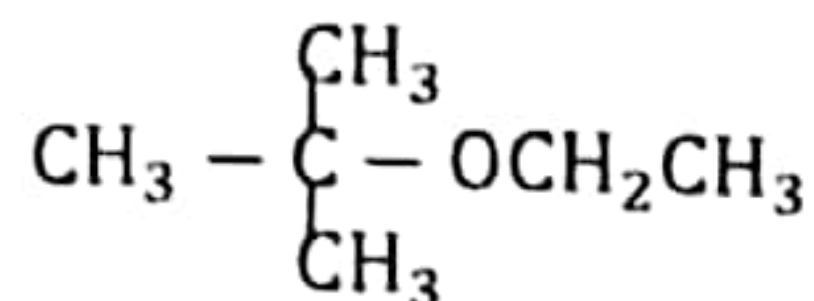
Haloalkanes can also be converted into ethers by heating with dry silver oxide as per the following equation. $2\text{CH}_3\text{CH}_2\text{Br} + \text{Ag}_2\text{O} \xrightarrow{\Delta} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + 2\text{AgBr}$

It should be noted that:

In the preparation of ether by this method, the alkoxide may be primary, secondary or tertiary but the haloalkane must be primary.

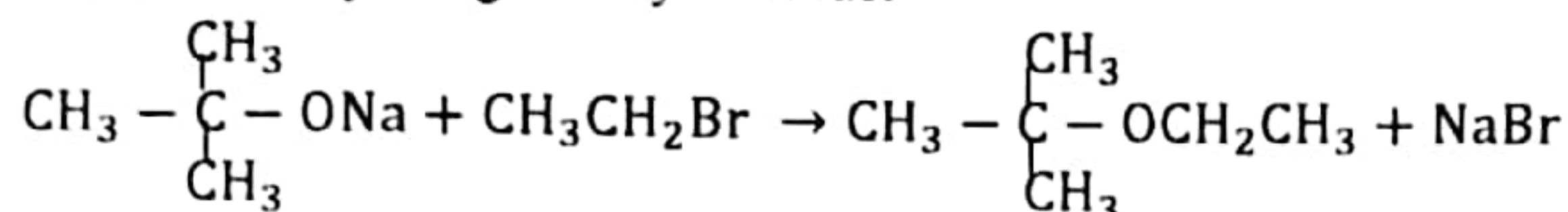
- This is simply because under presence of the alkoxide which is very strong base, secondary and tertiary haloalkane prefer of undergoing elimination reaction to nucleophilic substitution reaction.

For example if one want to prepare the compound shown below by Williamson's synthesis, may think one of the following route:

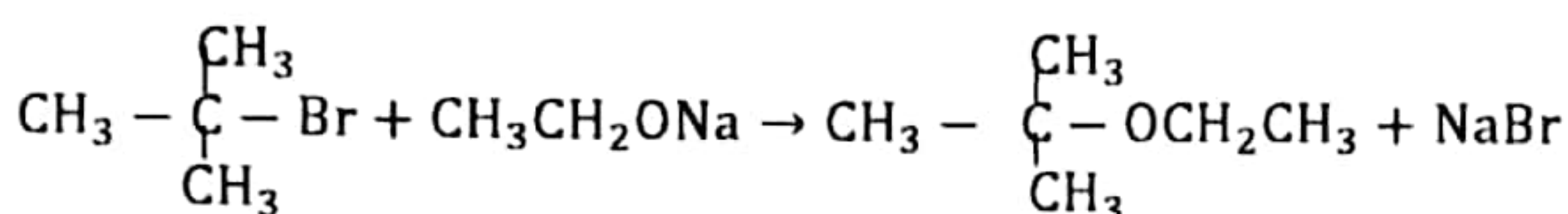


Targeted compound to be prepared by Williamson's synthesis

First route: By using tertiary alkoxide.

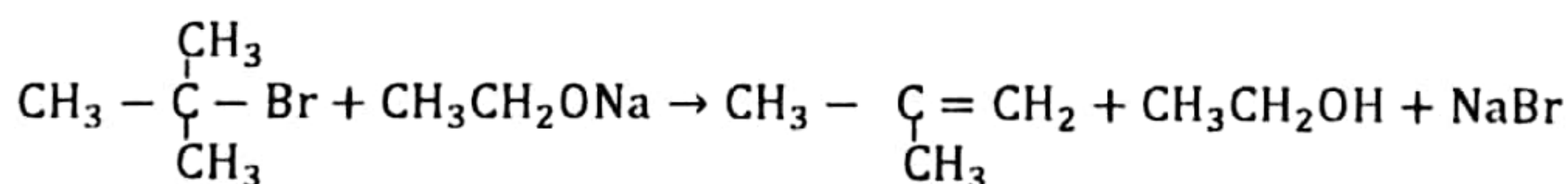


Second route: By using tertiary haloalkane



However in the second route ,the haloalkane being tertiary is more likely to undergo elimination reaction than substitution reaction as suggested.

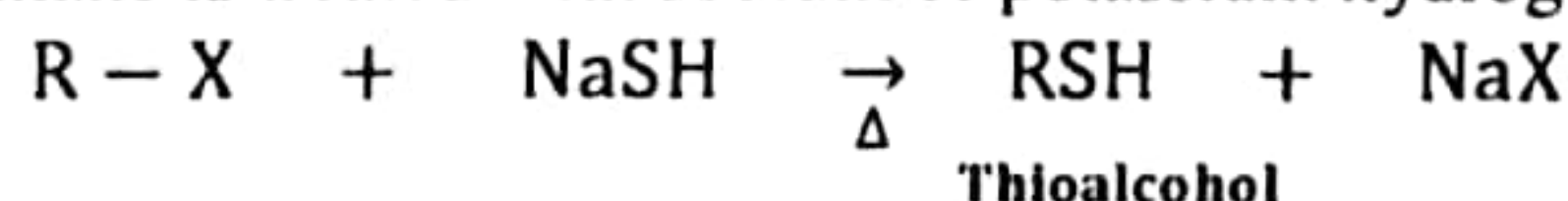
- So the second route is incorrect and the following elimination reaction will take place instead of nucleophilic substitution reaction.



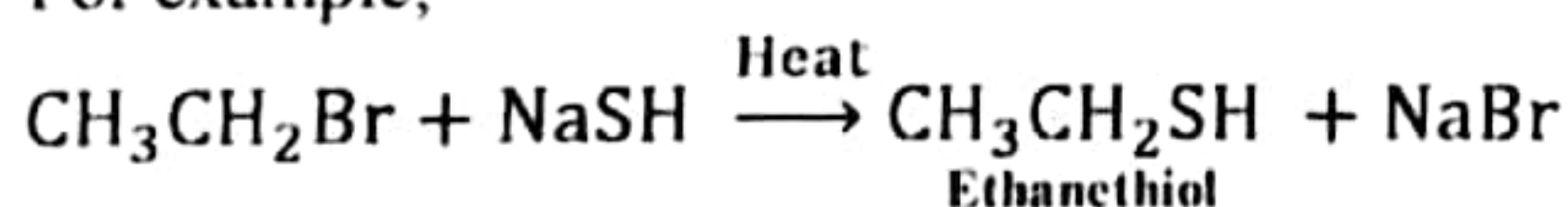
Elimination reaction(More preferred in the second route)

6. Substitution by hydrosulphide group

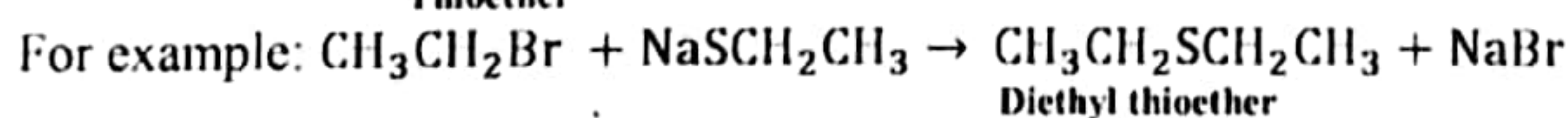
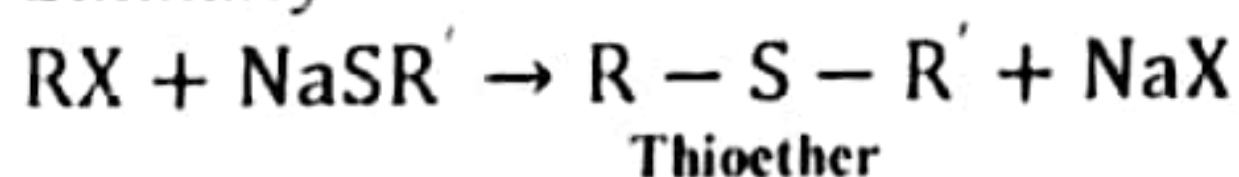
When haloalkane is treated with sodium or potassium hydrogen sulphide, thioalcohol or simply thio is formed.



For example;

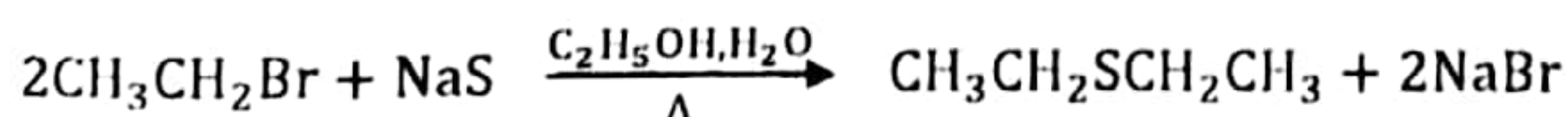


Similarly



It should be understood that;

Thioethers can also be formed by heating haloalkane with sodium or potassium sulphide



7. Alkyne formation

Haloalkanes react with alkynide to give alkyne

Generally: $RX + R'C \equiv CM \rightarrow R'C \equiv CR + MX$

Where M' is strong electropositive metal like Na and K.

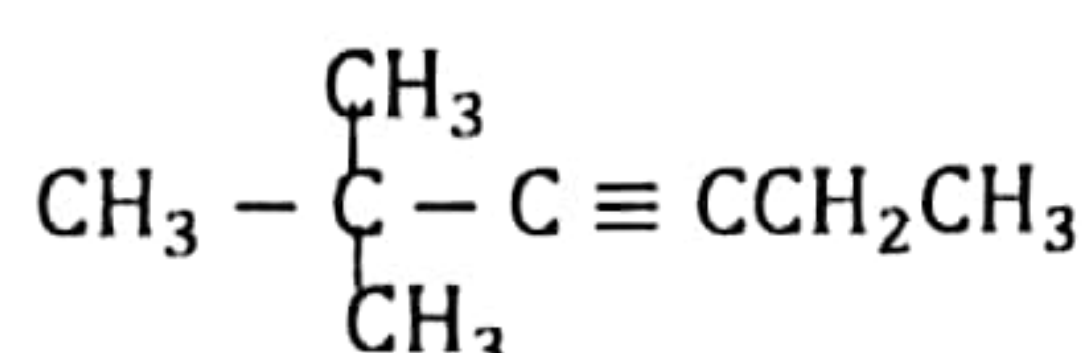
For example: $CH_3CH_2Cl + CH_3CH_2C \equiv CNa \rightarrow CH_3CH_2C \equiv CCH_2CH_3 + NaCl$

Again...!

In the preparation alkyne by this method, the alkynide may be primary, secondary or tertiary, but the haloalkane must be primary.

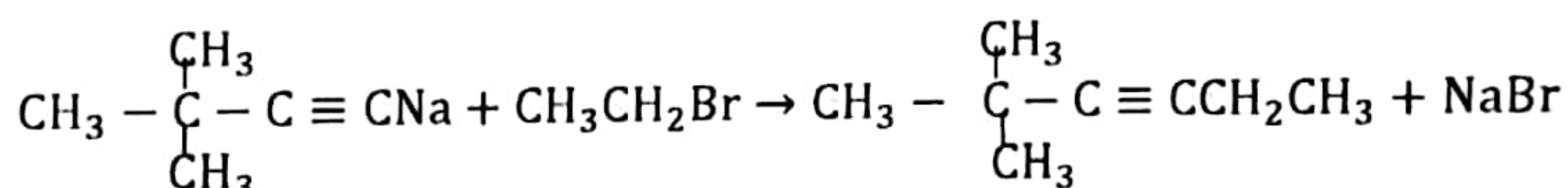
- Reasons for this are similar to those given for Williamson's synthesis.

For example, if one want to prepare the following compound by alkylation of alkynide (acetylidyde) ion.

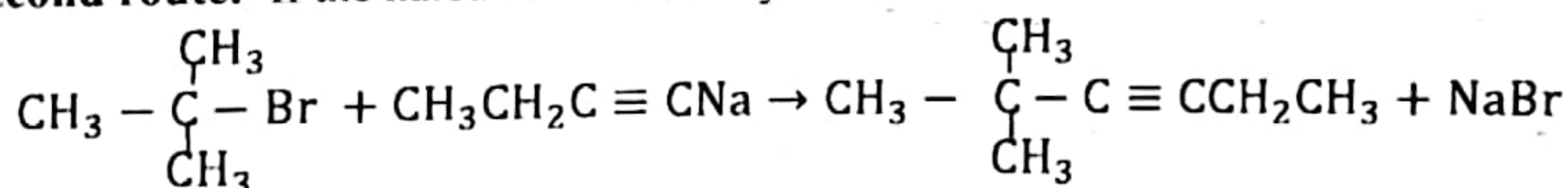


- The following routes may be considered in the preparation of the above compound.

First route: If the alkynide is tertiary.

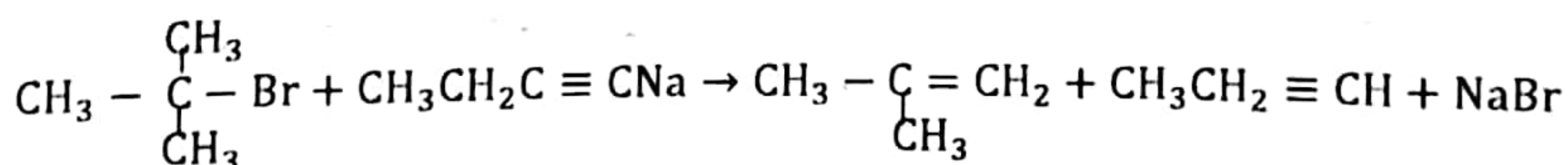


Second route: If the haloalkane is tertiary



Again in the second route, haloalkane being tertiary is more likely to undergo elimination reaction.

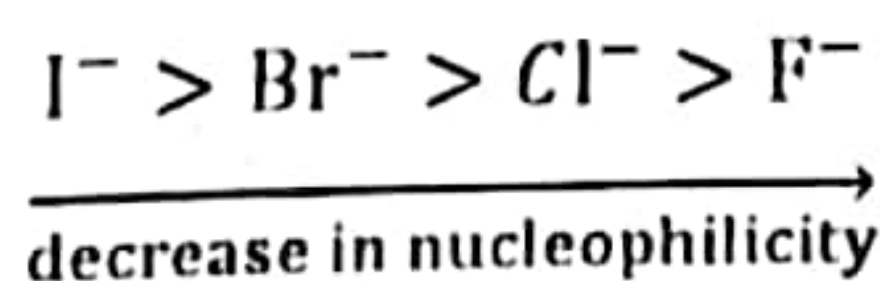
- So the second route is incorrect and the following elimination reaction will take place.



8. Replacement by another halogen

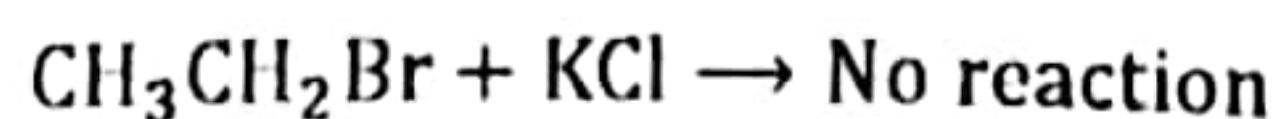
Halogen in haloalkane can be replaced by another halogen which is stronger nucleophilic.

- The strength of nucleophilic character of halogens is according to the following order:



For example; $CH_3CH_2Br + KI \rightarrow CH_3CH_2I + KBr$

But;

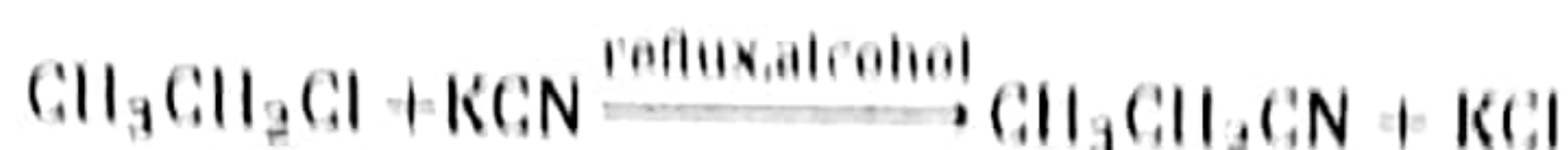


9. Formation of nitrile

Generally;



Example;



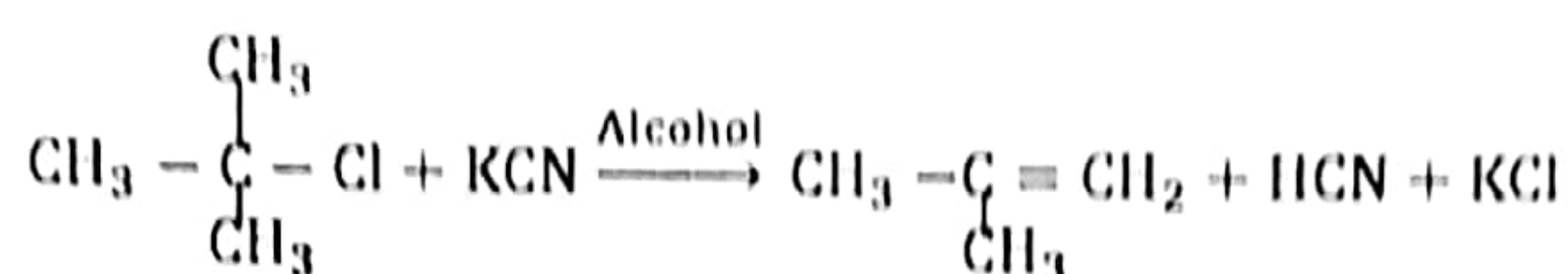
The reaction between haloalkane and the cyanide must take place in alcoholic medium and not aqueous medium because under aqueous medium the cyanide would undergo anionic hydrolysis to give hydroxyl ion (OH^-) which would react with the haloalkane to give alcohol.



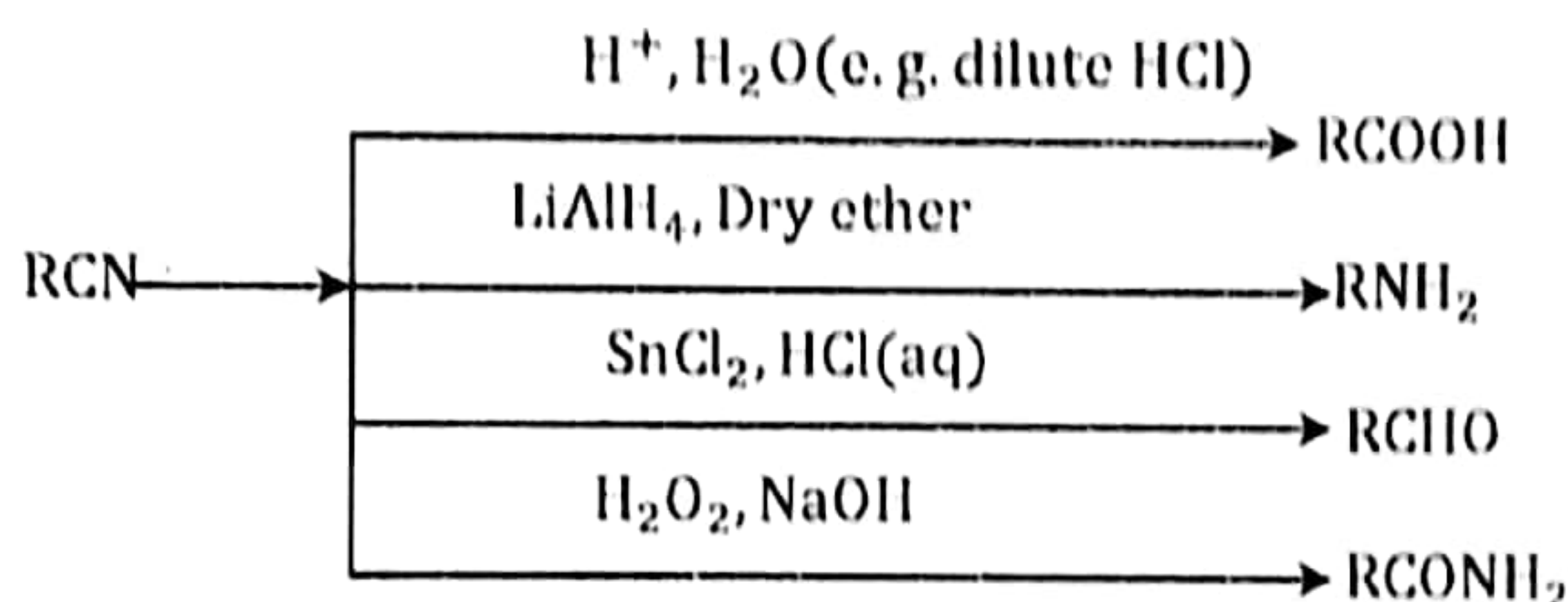
Again the reader should understand that:

The formation of nitrile by this method is limited for primary haloalkane only because CN^- is a very strong base and therefore with secondary and tertiary haloalkane it tends to form alkenes (elimination product) rather than nucleophilic substitution product (nitrile).

For example

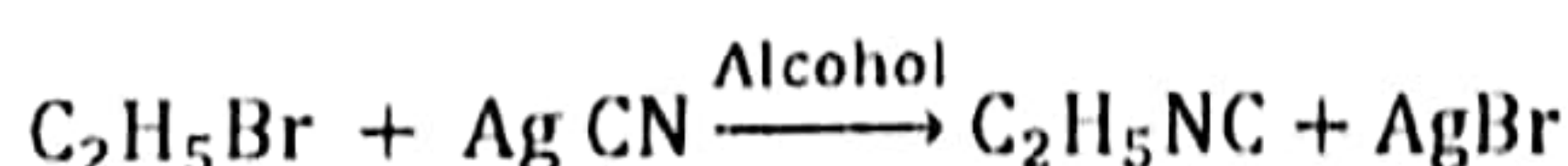


Nitrile is used to synthesize various organic compounds as shown below.



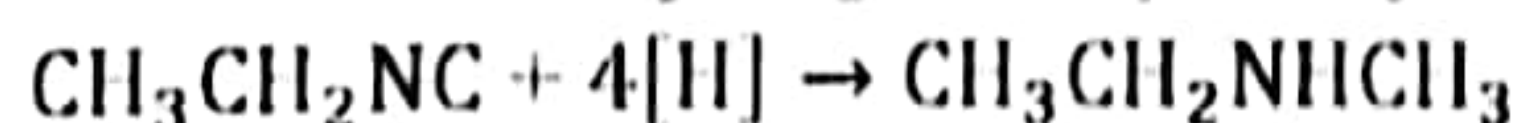
So the reaction (formation of nitrile) is very important in dealing with conversion problems which show that number of carbons has been increased by one.

But;



Where $\text{C}_2\text{H}_5\text{NC}$ is isocyanides and is recognised by its **unpleasant smell**.

- On reduction with nascent hydrogen, alkyl isocyanides give secondary amines.



Where $[\text{H}]$ stands for nascent hydrogen, commonly from $\text{Na/C}_2\text{H}_5\text{OH}$ mixture or hydrogen atoms from reducing agent, mainly LiAlH_4 for this case.

Be careful!

NaBH_4 (even Sn/HCl mixture) is not a powerful reducing agent enough to reduce nitrile or isonitrile into amine.

Example 1

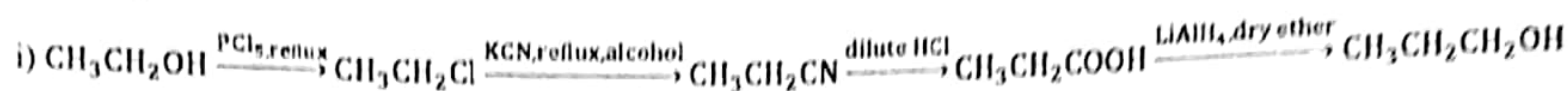
Show how the following conversions can be achieved.

- $\text{CH}_3\text{CH}_2\text{OH}$ into $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Ngaiza's series of advanced chemistry

ii) $\text{CH}_3\text{CH}_2\text{Cl}$ into $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ iii) $\text{CH}_3\text{CH}_2\text{OH}$ into $\text{CH}_3\text{CH}_2\text{COOH}$ iv) CH_3CH_3 into $\text{CH}_3\text{CH}_2\text{CH}_3$

Answer



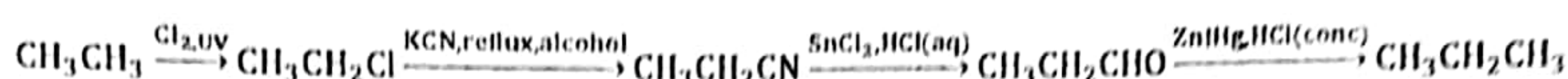
ii)



iii)



iv)

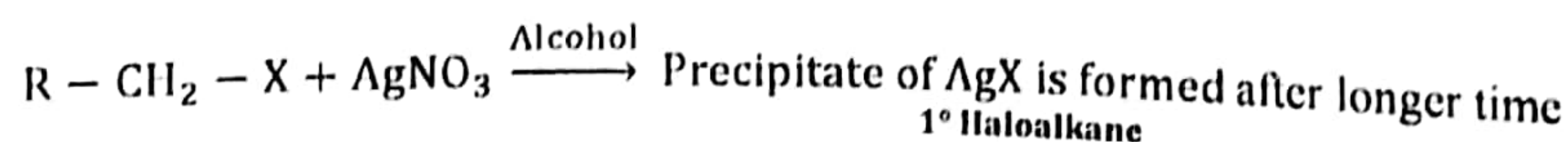
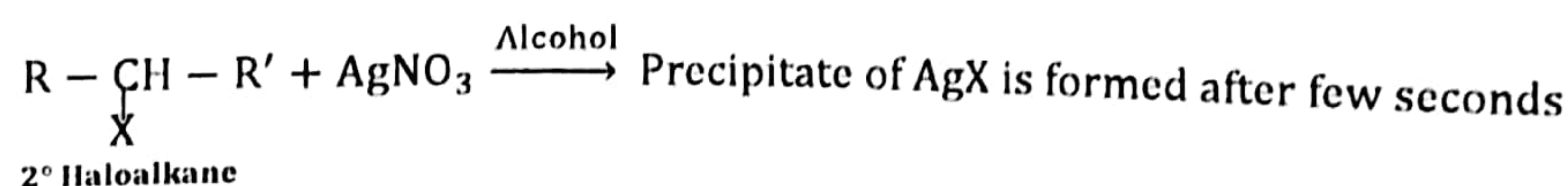
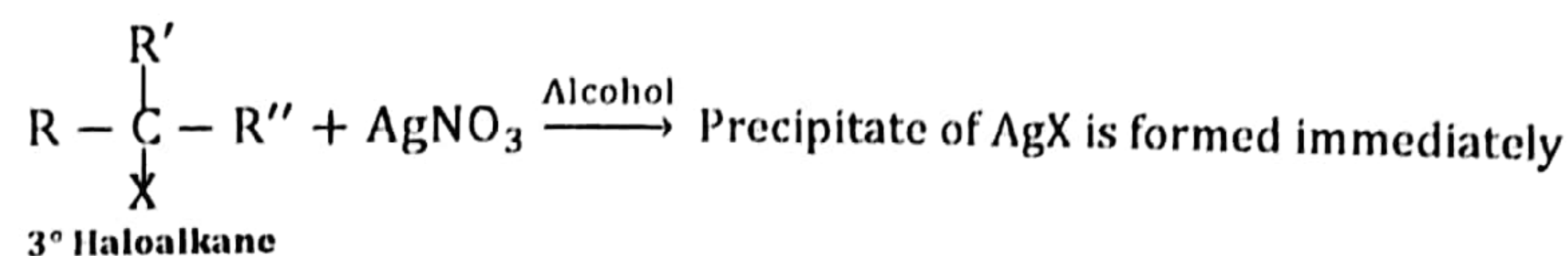


A chemical test to distinguish between primary, Secondary and tertiary haloalkane

Different classes of haloalkanes may be differentiated by treating the compound with solution of alcoholic silver nitrate and then considering rate of forming precipitate of silver halide based on the difference of their reactivity.

- The tertiary haloalkane being most reactive produce precipitate of silver halide immediately.
- The secondary haloalkane produce slight precipitate after a few seconds. The precipitate thickens up with time.
- The primary being least reactive, takes longer time to produce precipitate of silver halide.

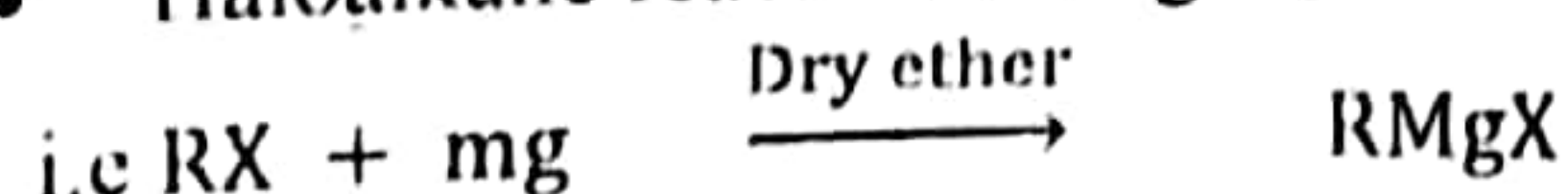
That is



Grignard reagent formation

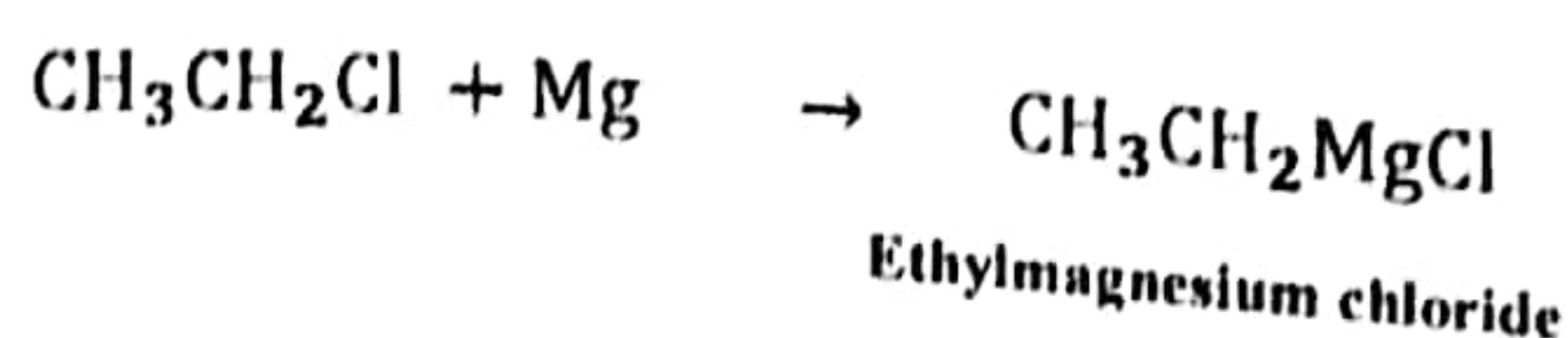
Grignard reagent is alkylmagnesium halide (RMgX)

- Haloalkane react with magnesium under presence of dry ether yielding grignard reagent.



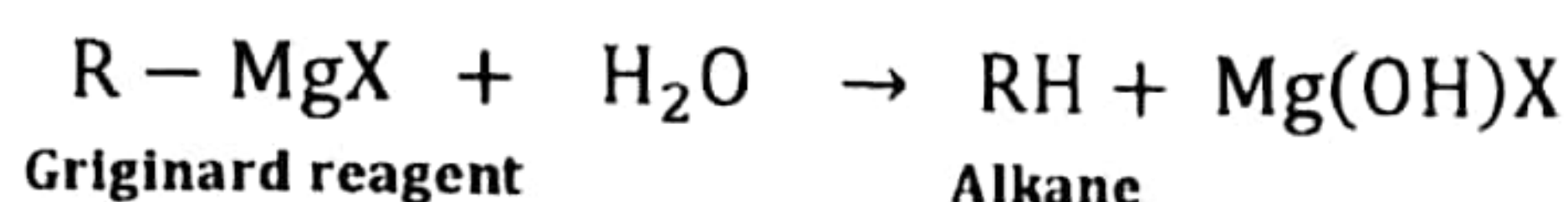
Grignard reagent

Example:

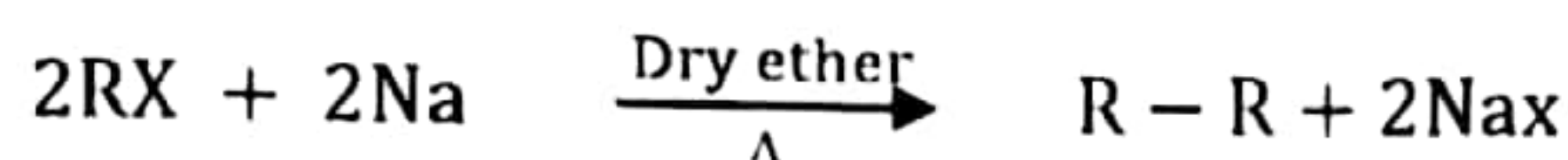


The reader should understand that:

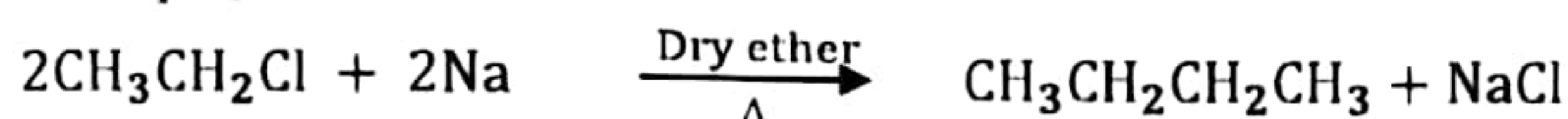
In preparation of Grignard reagent by this method, the ether must be dry because the Grignard reagent is so reactive that would reacts with water (in the ether solution to give alkane as per equation);

**Wurtz reaction**

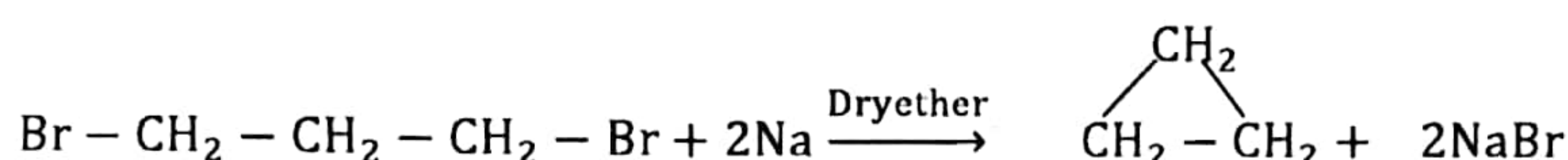
Generally:



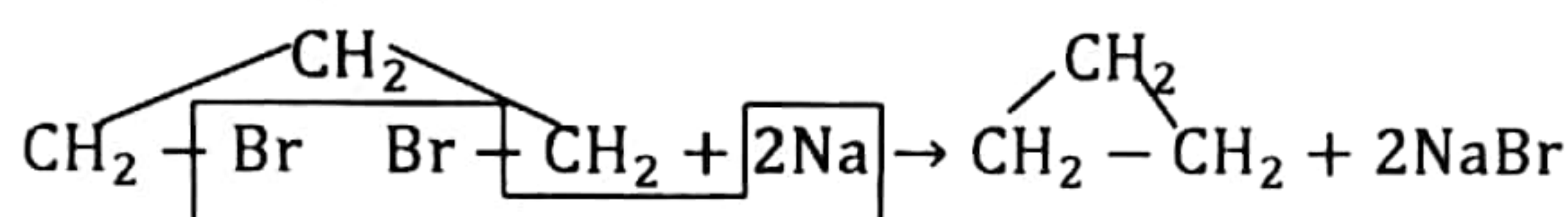
Example;



But;

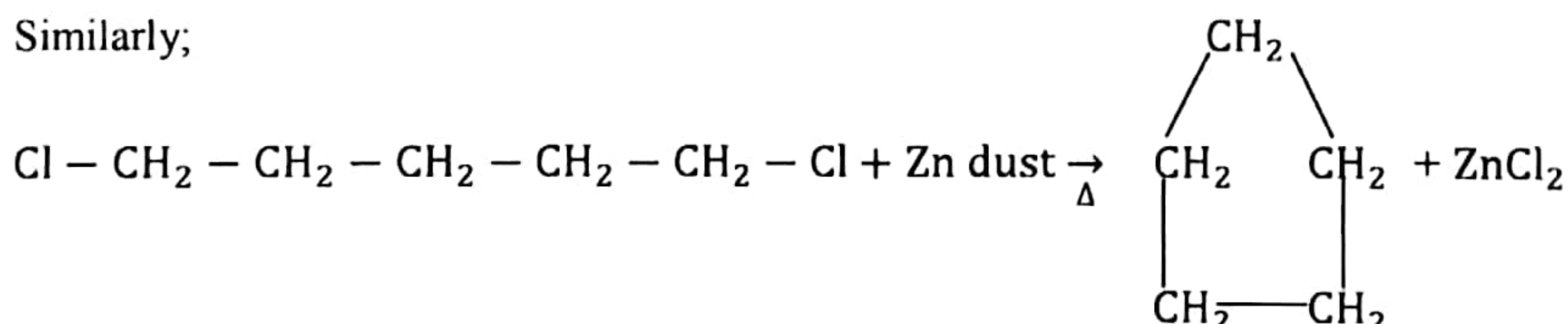


Memorising:

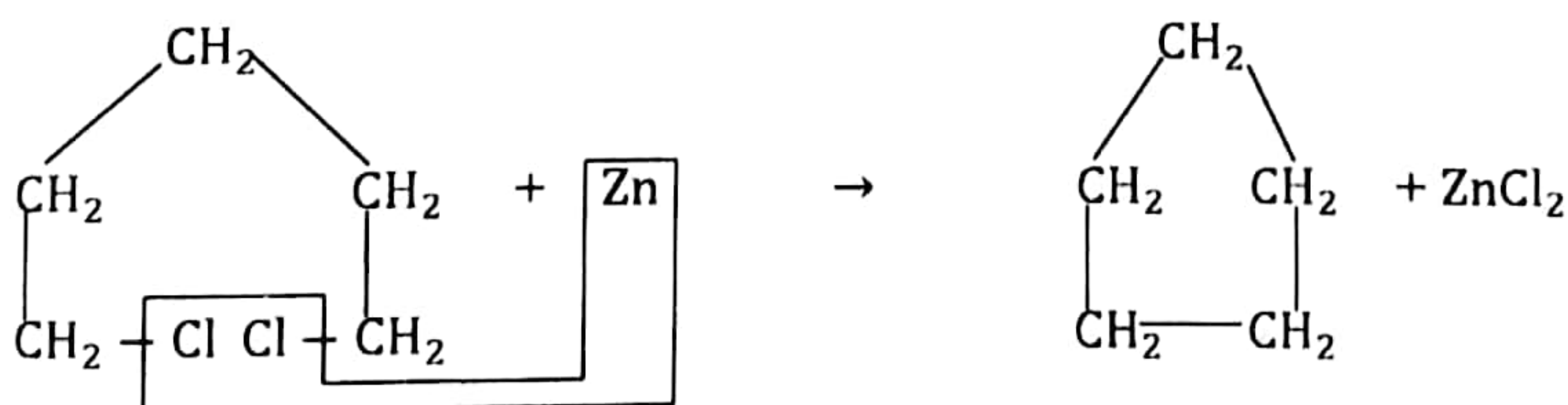


This reaction may be regarded as **intramolecular Wurtz reaction** and is known as **Freund reaction**.

Similarly;

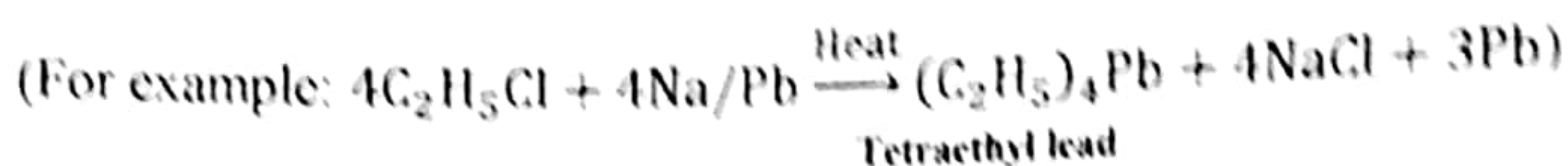


Memorising:

**Attention!**

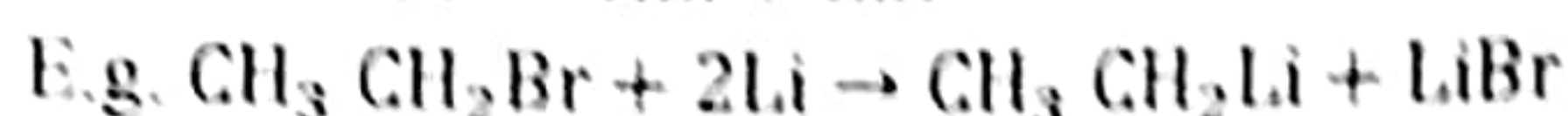
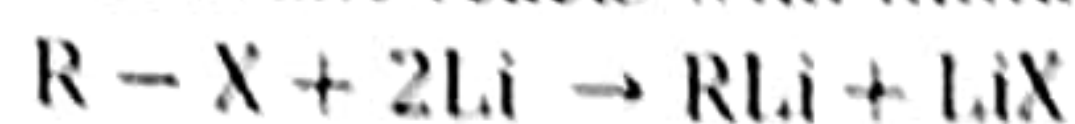
Haloalkane, RX reacts with metals to give different products depending on the kind of metal which is used:

- (i) $2\text{R} - \text{X} + 2\text{Na} \xrightarrow{\text{Dry ether}} \text{R} - \text{R} + 2\text{NaX}$
- (ii) $\text{R} - \text{X} + 2\text{Li} \xrightarrow{\text{Dry ether}} \text{RLi} + \text{LiX}$
- (iii) $2\text{C}_2\text{H}_5\text{Br} + 2\text{Zn} \xrightarrow{\text{Dry ether}} (\text{C}_2\text{H}_5)_2\text{Zn} + \text{ZnBr}_2$
Bromoethane Frankland reagent
- (iv) $\text{R} - \text{X} + \text{Mg} \xrightarrow{\text{Dry ether}} \text{RMgX}$
- (v) $4\text{R} - \text{X} + 4\text{Na/Pb} \xrightarrow{\text{Heat}} \text{R}_4\text{Pb} + 4\text{NaCl} + 3\text{Pb}$



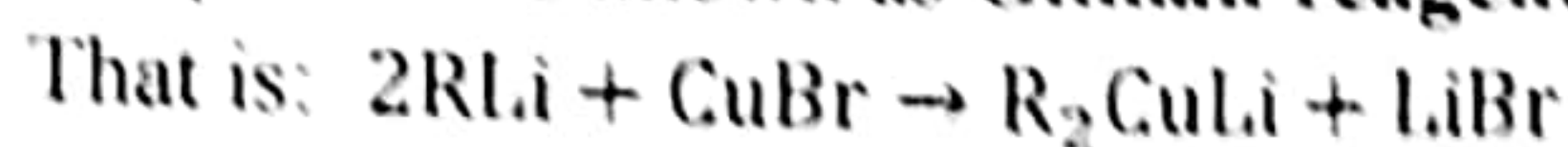
It should be understood that:

When haloalkane reacts with lithium to form alkyl lithium as per equation:

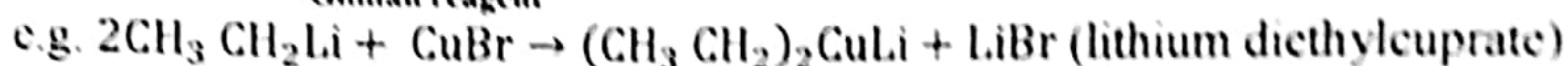


Ethyl lithium

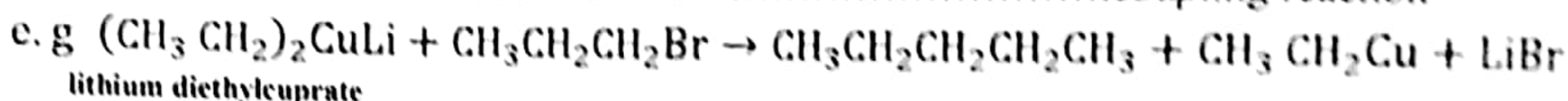
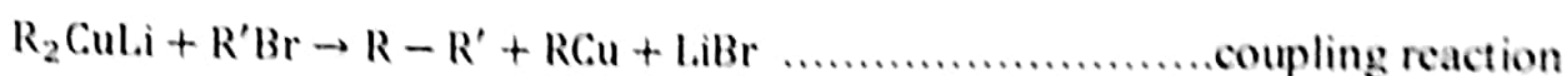
– The alkyl lithium can react with copper(I) halide (like CuI and CuBr) to form R_2CuLi and the product is known as **Gilman reagent**.



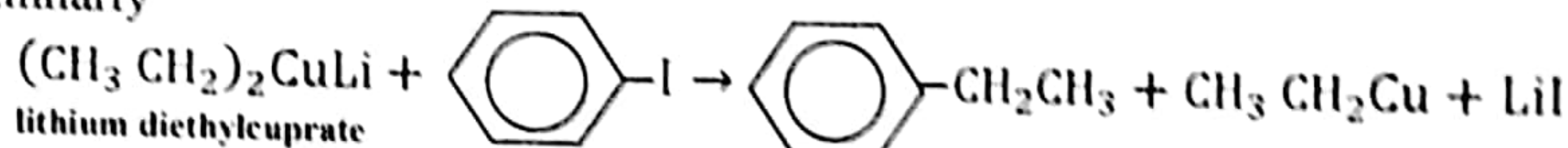
Gilman reagent



Gilman reagent undergoes coupling reaction with alkyl halide (haloalkane like RI and RBr) to give alkane; That is:

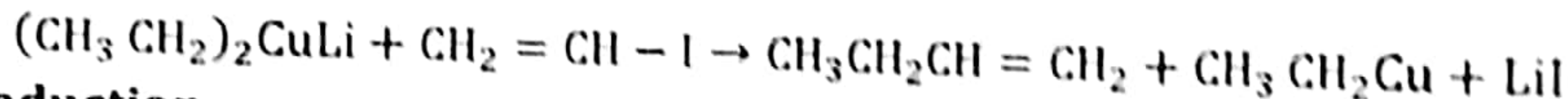


Similarly



lithium diethylcuprate

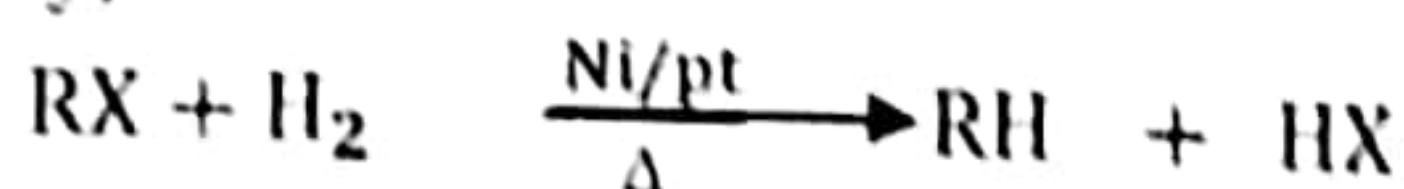
Or



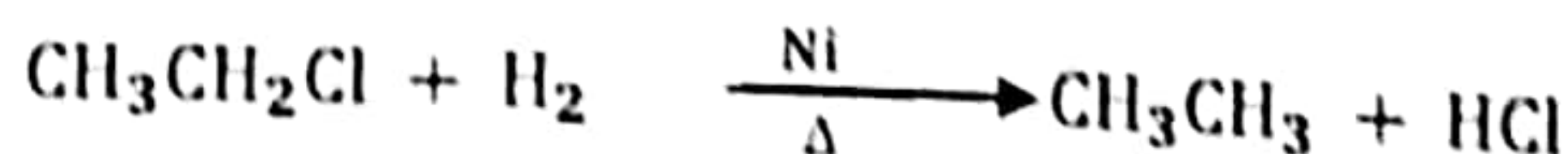
Reduction

With hydrogen gas under presence of nickel or platinum catalysts and heat alkane is formed from haloalkene.

Generally;

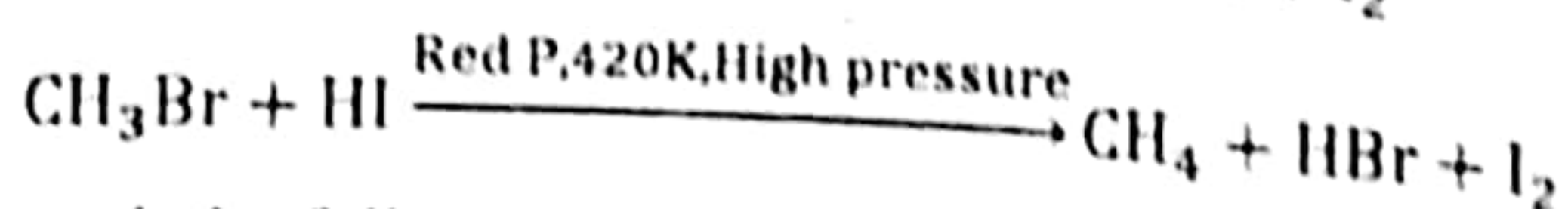
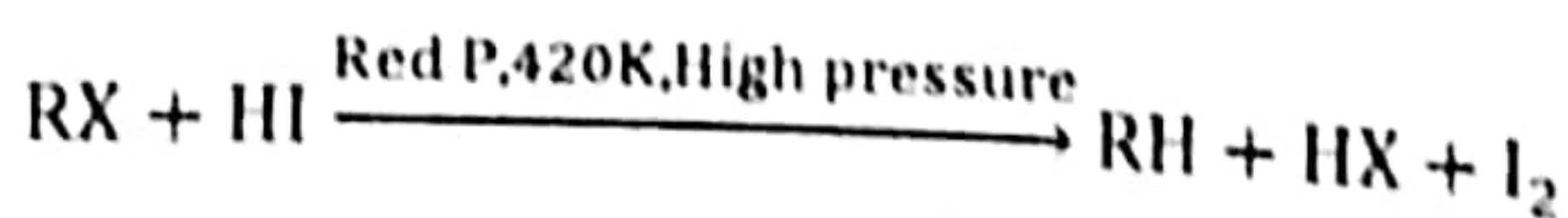


Example



The reader should understand that:

Hydroiodic acid is powerful reducing agent which reduces haloalkanes to alkanes at **420K** in presence of **red phosphorous**.



You may ask the following questions from the above reaction:

- The reaction is carried out under high pressure, why?
- What is the use of red phosphorous in the above reaction?

Don't worry; here are answers of your questions!

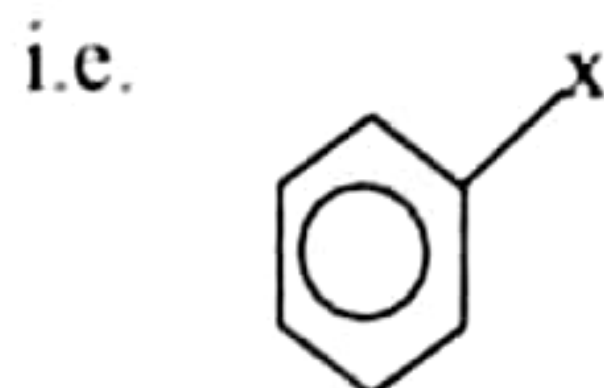
- Because HI has lower boiling point (399K) at 1atm (atmospheric pressure). So in presence of the large pressure, its boiling point is raised and it become above 399K as well as above 420K easier.

- (ii) To prevent occurrence of reverse reaction by combining with liberated iodine which would react with alkane to form reverse reaction. $2P + 3I_2 \rightarrow 2PI_3$

HALOARENE

This is the halohydrocarbon which is formed when at least one hydrogen atom of benzene is replaced by halogen.

- The simplest one is formed when only one hydrogen atom of benzene is replaced by halogen



Chemical reactions of haloarenes

This includes;

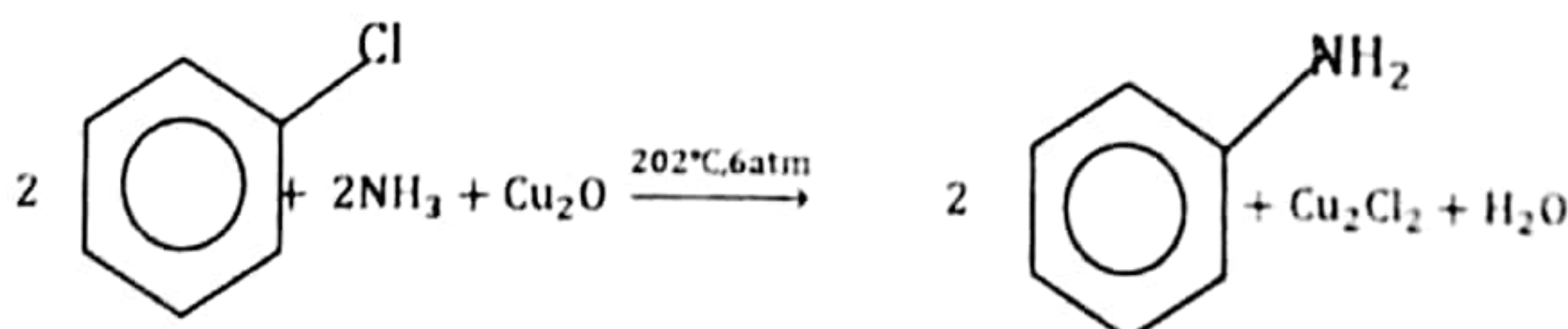
- Nucleophilic substitution reactions
- Grignard reagent formation
- Wurtz/Fittings or coupling reaction
- Reaction with copper powder
- Reduction
- Electrophilic substitution reactions

Nucleophilic substitution reaction

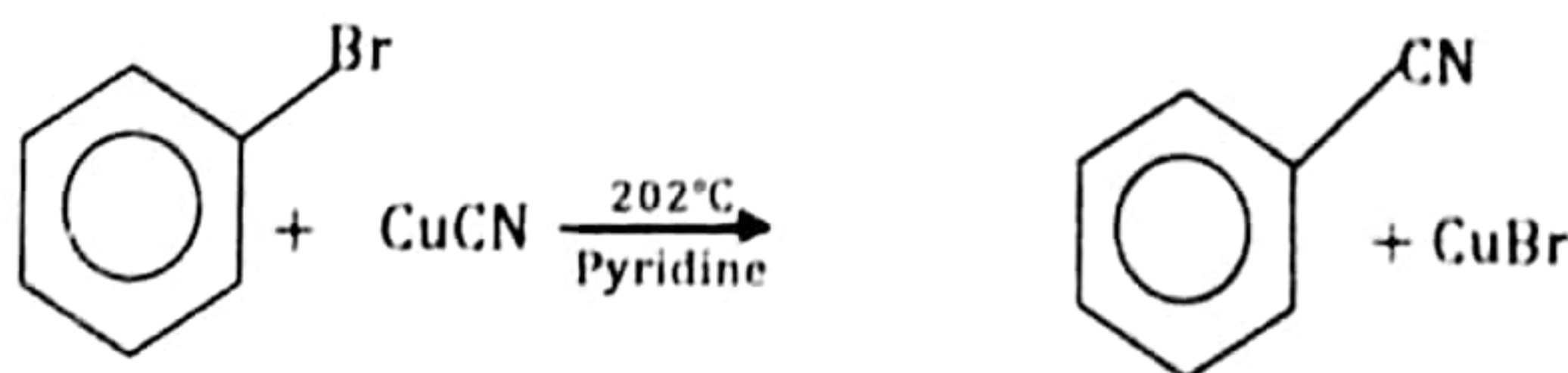
Compared to aliphatic haloalkane, haloarene is less reactive towards nucleophile in nucleophilic substitution reaction due to mesomerism which lead to formation of double bond, $C = Cl$ that is more difficult to break than $C - Cl$ in aliphatic haloalkane.

- For example;

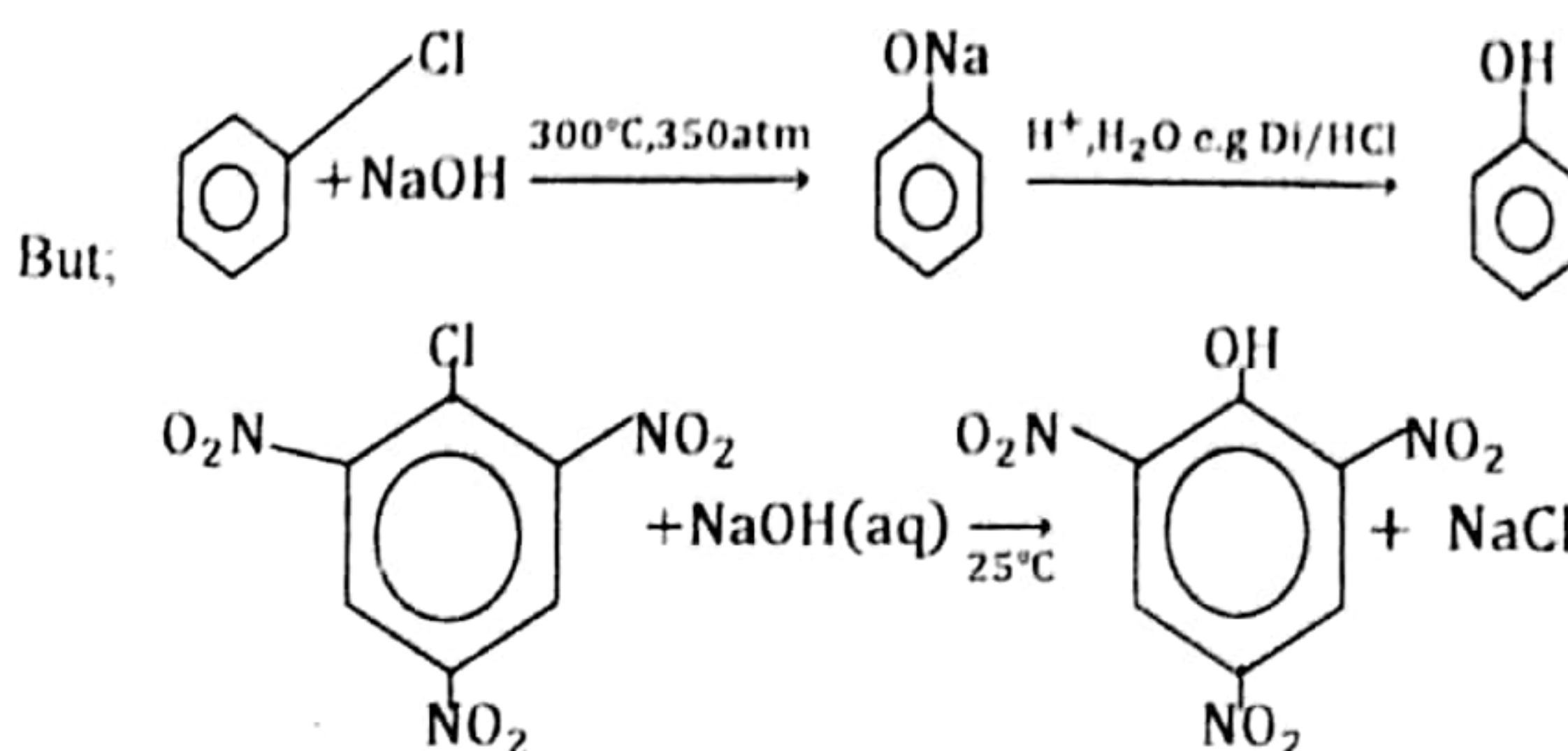
(i)



(ii)



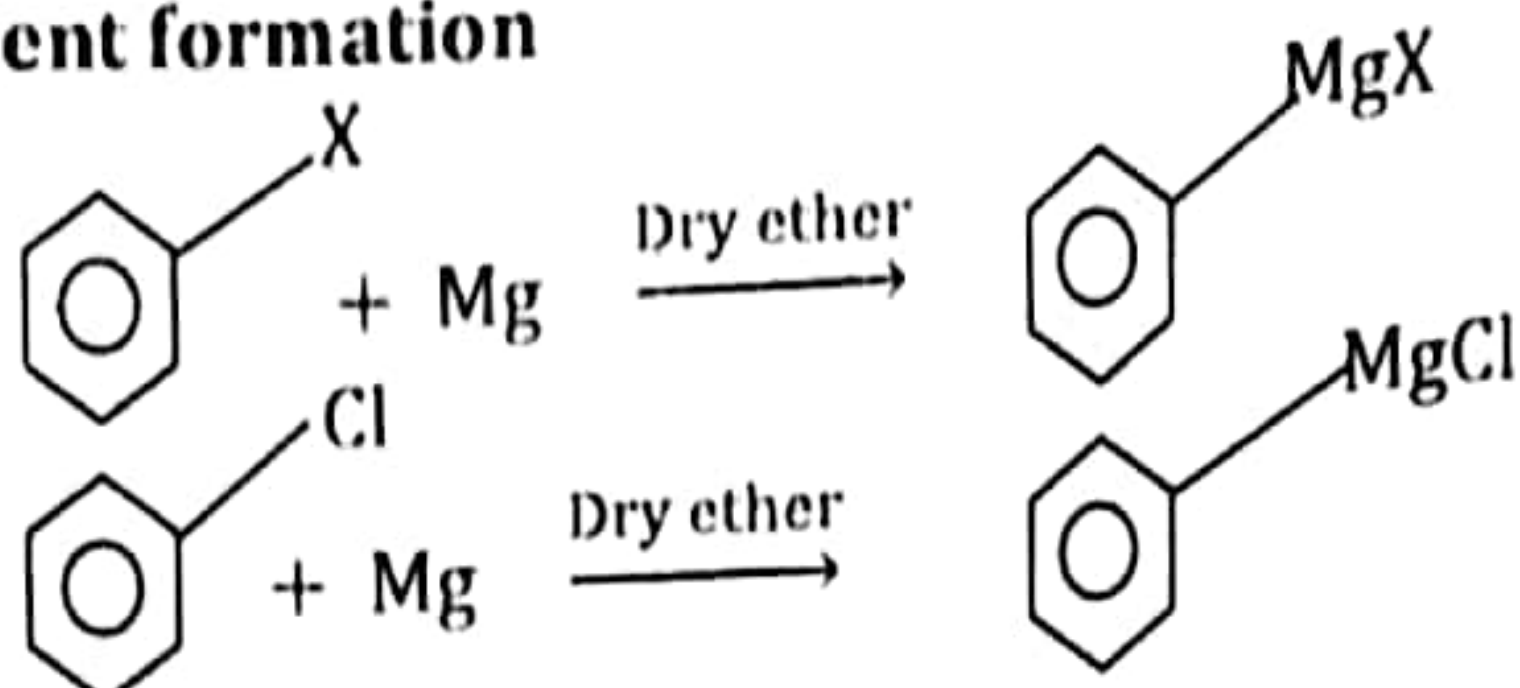
(iii)



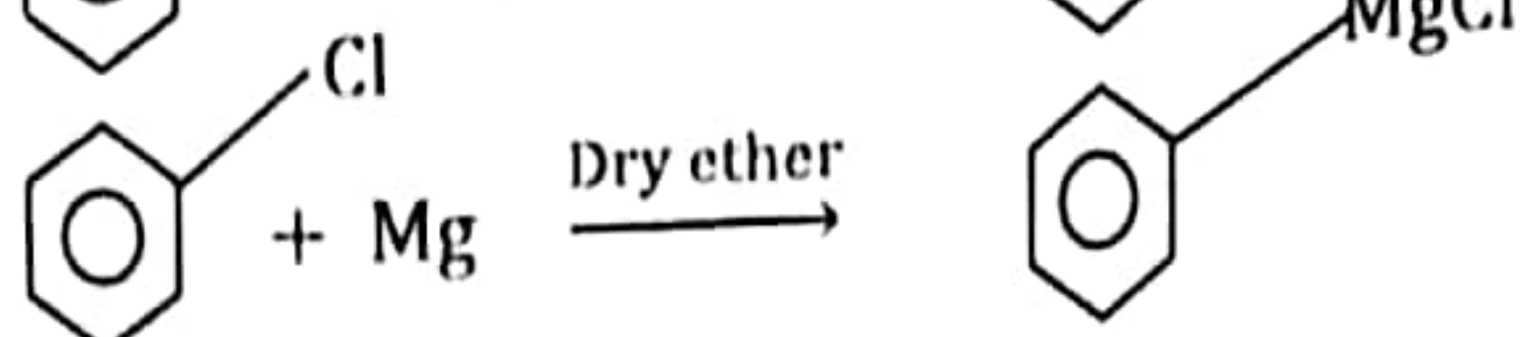
(Here direct substitution of Cl is possible at room temperature because presence of electron withdrawing groups NO_2 , in benzene ring makes the compound more reactive towards nucleophile, OH^- , in the nucleophilic substitution reaction)

Grignard reagent formation

Generally:

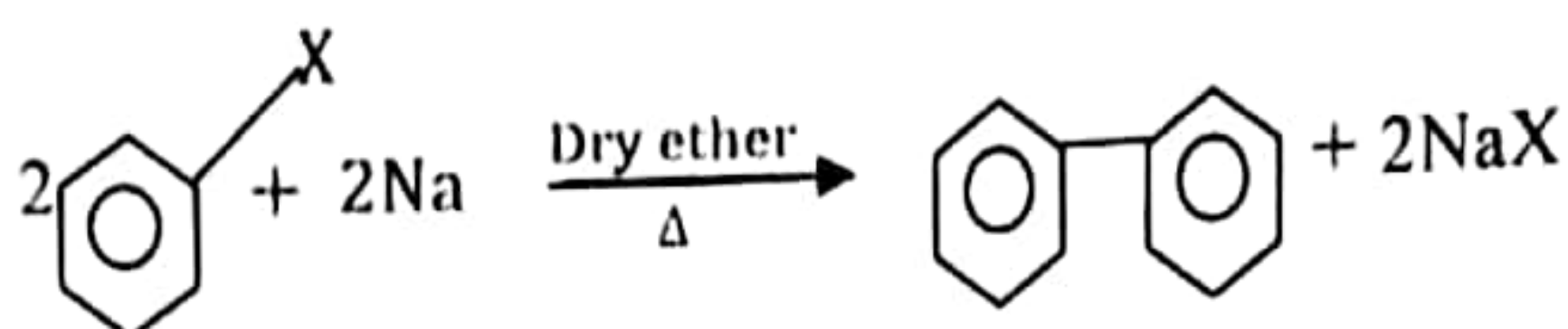


Example;

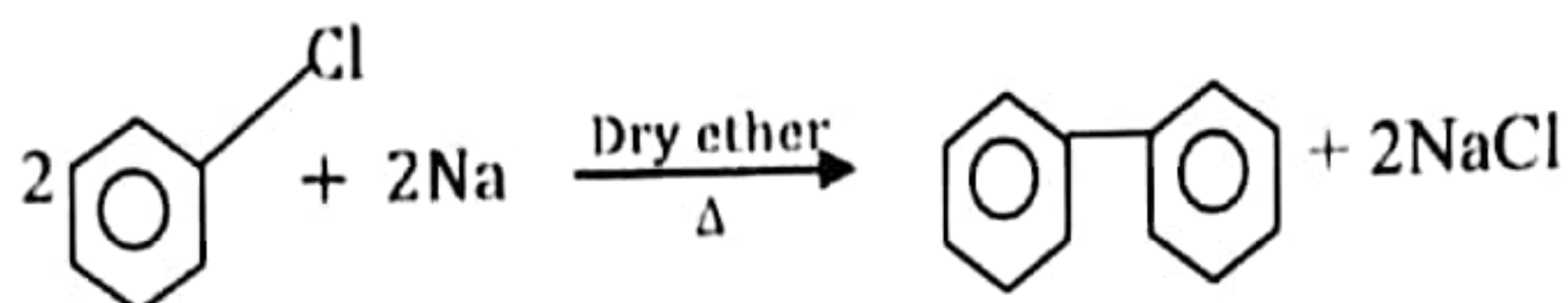


Wurtz reaction

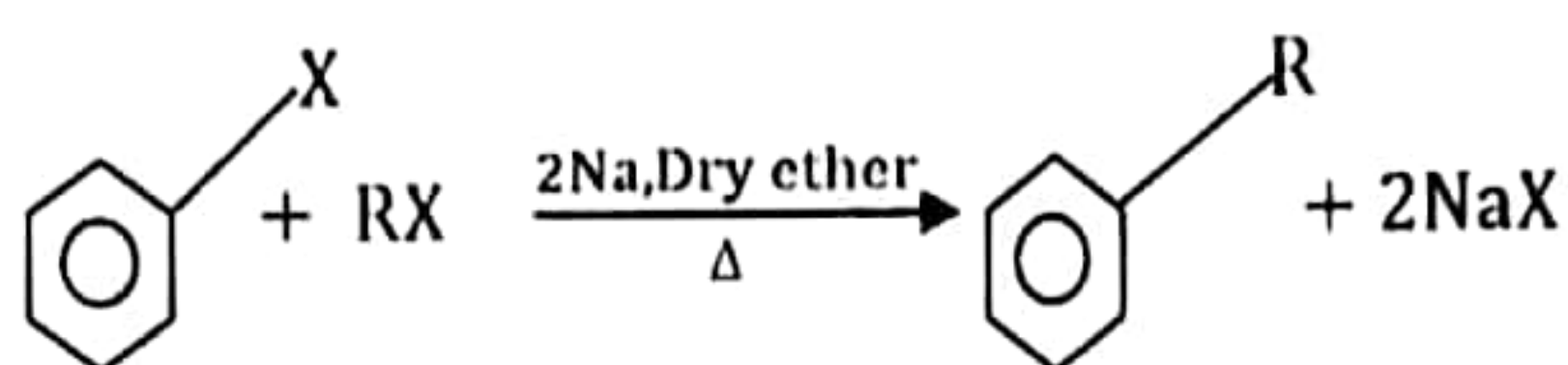
Generally:



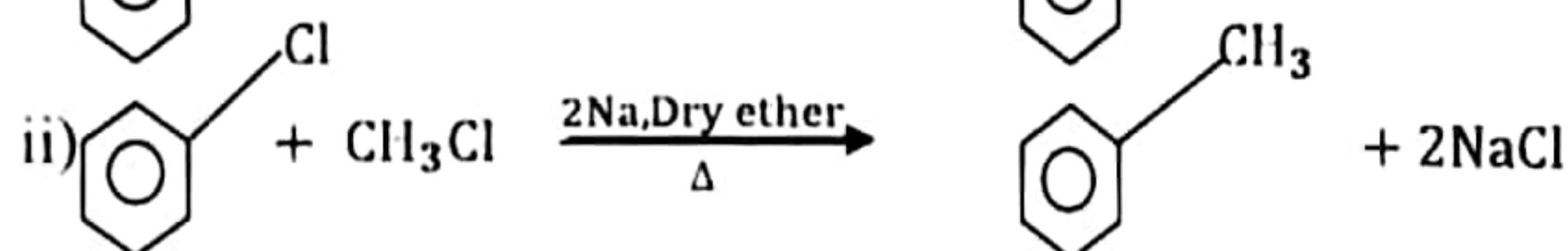
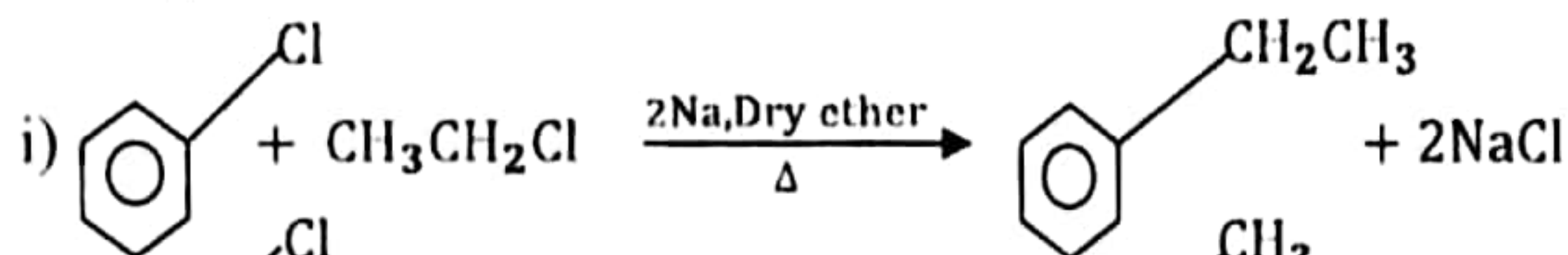
Example;



Similarly;

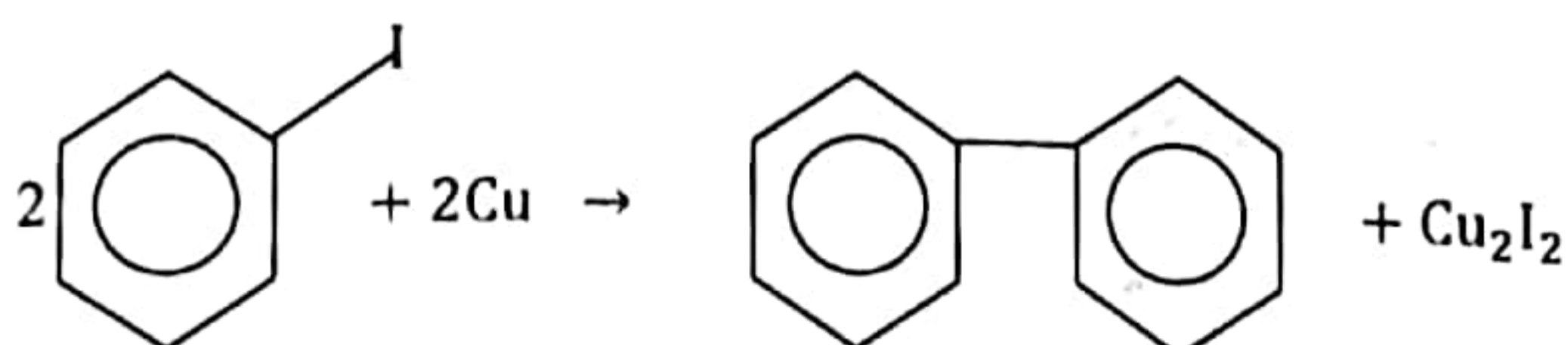


Example:



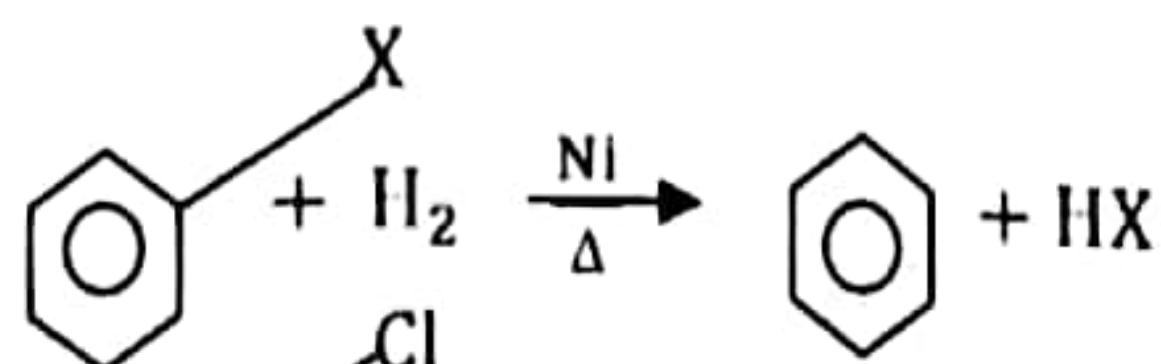
Reaction with copper powder (Ullmann reaction)

Iodobenzene reacts with copper powder under presence of heat to give diphenyl

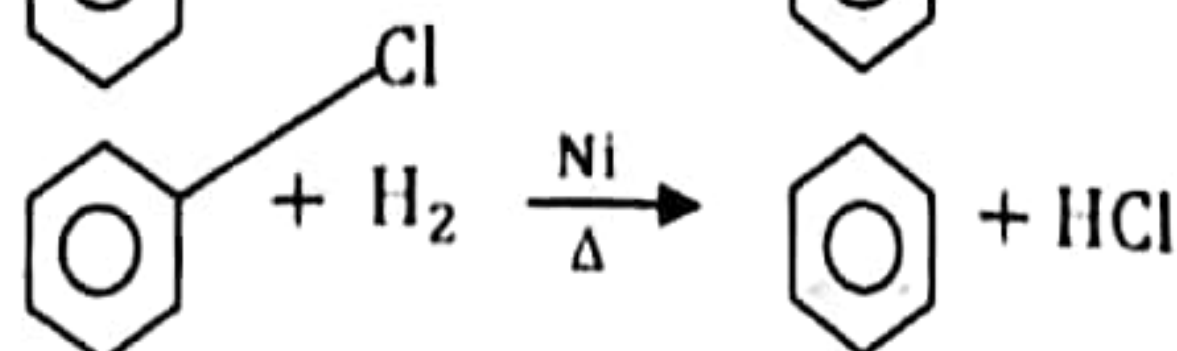


Reduction

Generally:



Example;

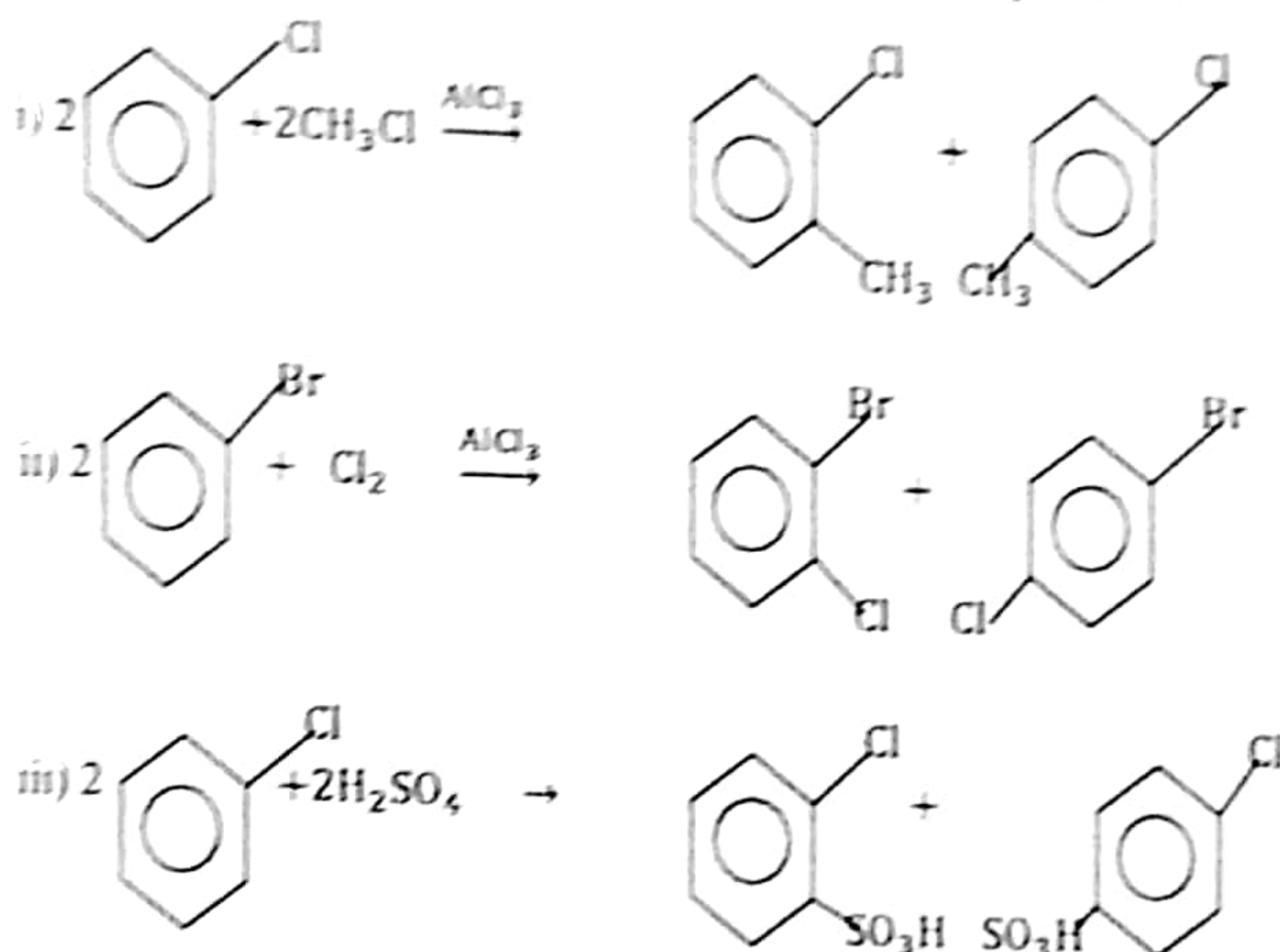


Note:

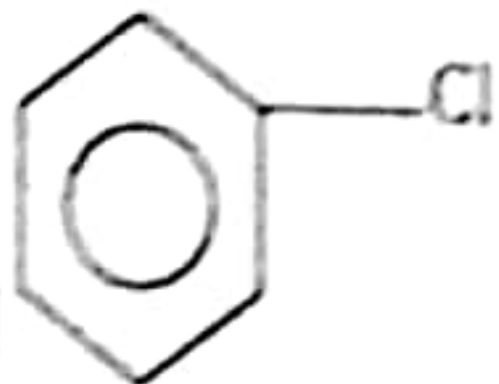
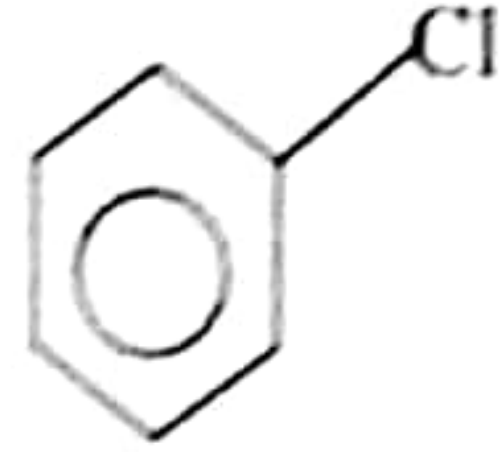
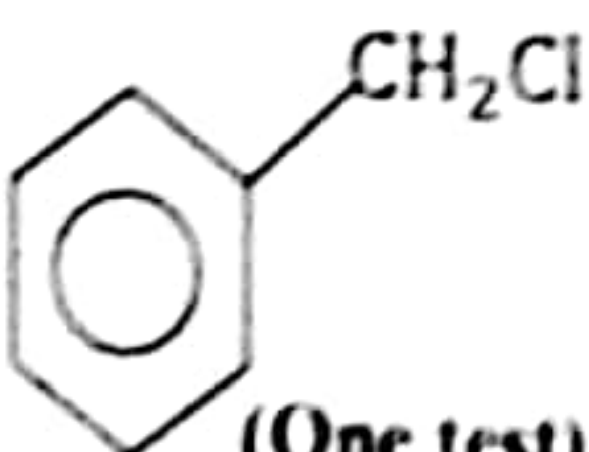
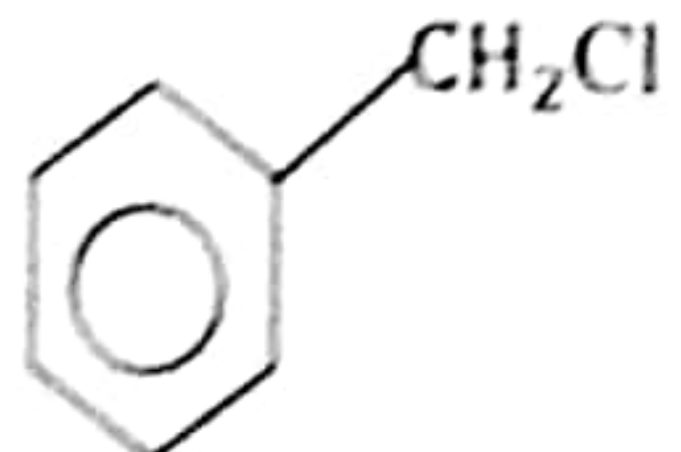
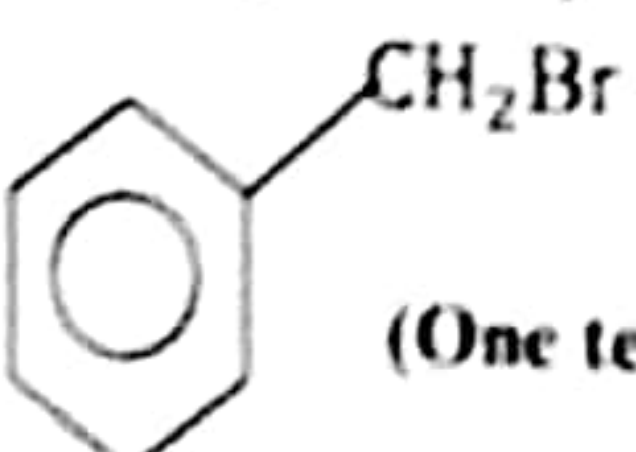
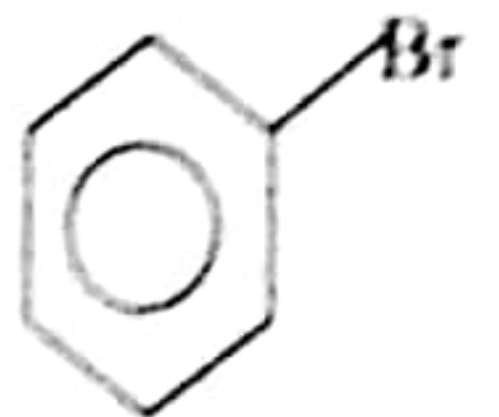
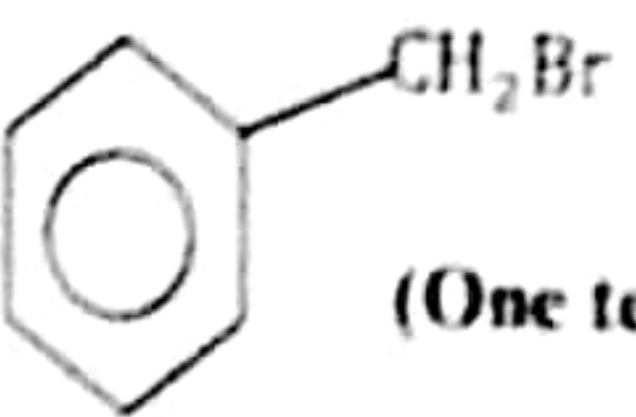
When hydrogen present in excess, cyclohexane is formed instead of benzene as a result of further hydrogenation of the later (benzene)

Electrophilic substitution reactions

Under this heading haloarene undergo similar reaction as those of benzene, the only difference is that halogen present in haloarene directs an incoming electrophile at ortho and para positions. Example.

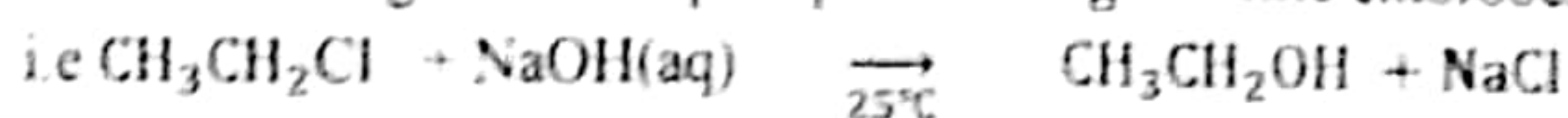
**Example 2**

Give chemical tests to distinguish each of the following pairs of organic compounds

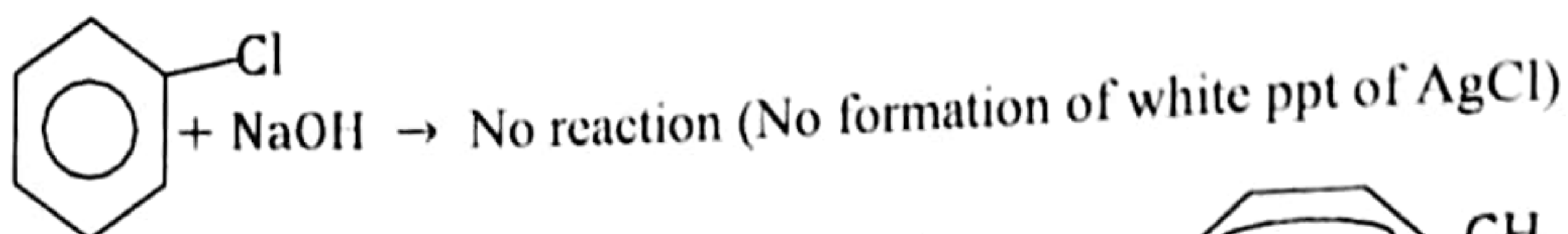
- (i) $\text{CH}_3\text{CH}_2\text{Cl}$ and  (one test)
- (ii)  and  (One test)
- (iii)  and  (One test)
- (iv) $\text{CH}_3\text{CH}_2\text{Br}$ and $\text{CH}_3\text{CH}_2\text{Cl}$ (One test)
- (v)  and  (One test)
- (vi) Chloroform and carbon tetrachloride (One test)

Solution

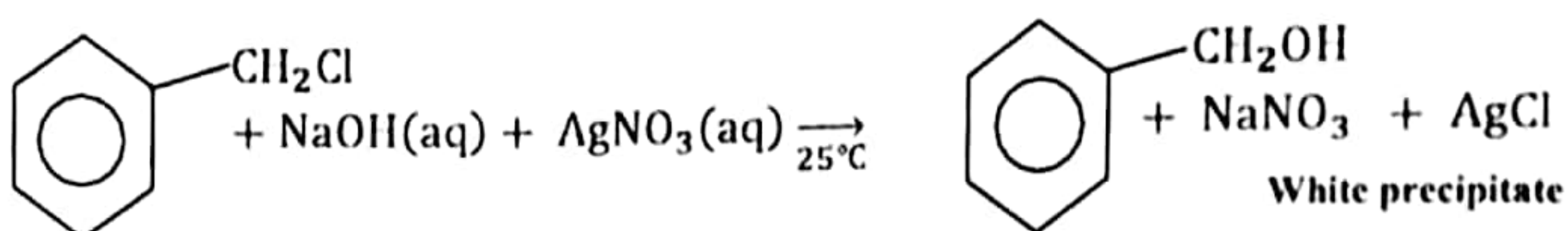
- i) With NaOH (aq) at room temperature (laboratory condition) followed by AgNO_3 (aq), chloroethane gives white precipitate of AgCl while chlorobenzene does not.



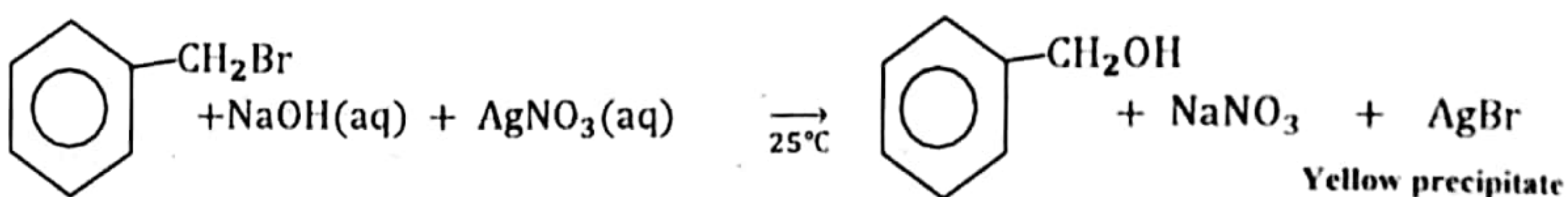
While



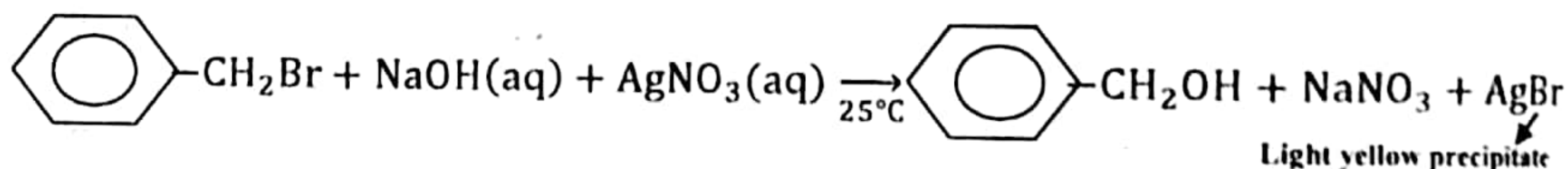
- ii) The solution is similar to (i) above where  will give white precipitate of AgCl (Its halogen is not directly bonded to benzene)
- iii) With NaOH(aq) at room temperature followed by addition of AgNO₃(aq), the first compound give white precipitate of AgCl while the later give light yellow (creamy) precipitate of AgBr.



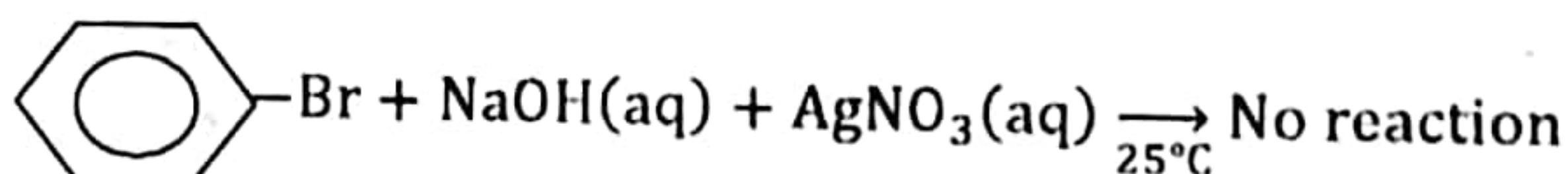
While



- iv) The same as (iii) above
- v) With solution of NaOH followed by addition of solution of AgNO₃ at room temperature, the second compound gives light yellow precipitate while the first one does not.



While



USES AND HAZARD OF HALOHYDROCARBONS

i) Solvents

Many small chlorinated molecules are useful organic solvents.

- These organic solvents like chloroform (CHCl₃) and dichloromethane (CH₂Cl₂) are immiscible in water.

Triethene (Cl₂C = CHCl) and tetraethene (Cl₂C = CCl₂) are used as solvents in dry-cleaning and as degreasing agents (to remove oil and grease) in metal and textile processing.

However the reader should understand that:

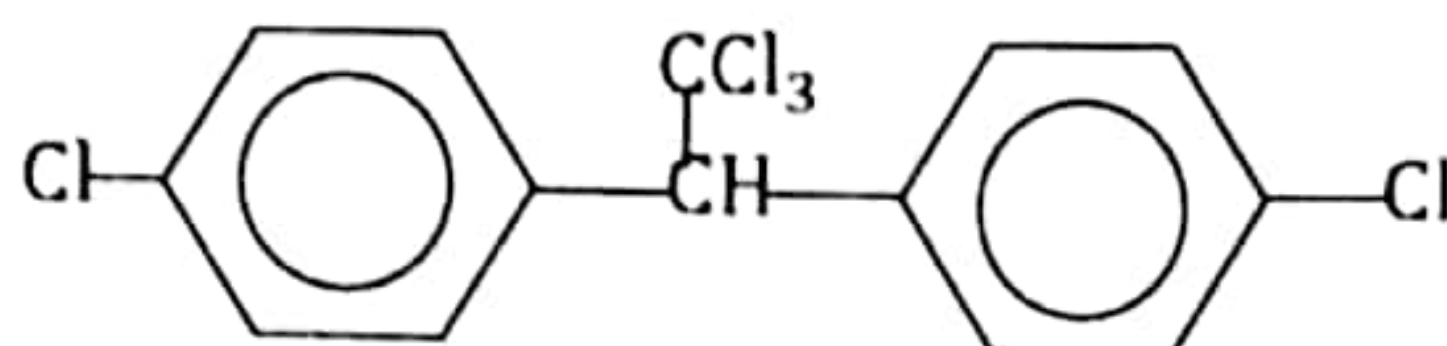
Most of these halohydrocarbons cause cancer. They are said to be **carcinogens** (substances capable of causing cancer in living tissue).

- So nowadays some of them like carbon tetrachloride CCl₄ have been banned as organic solvent in the laboratory.

ii) Insecticides and herbicides

Insecticides is a substance used for killing insects.

- Some hydrocarbons, mainly DDT have been found to have insecticidal properties.
- The structure of DDT is shown below



Common name: dichlorodiphenyltrichloroethane (DDT)

IUPAC name : 1,1,1 – trichloro – 2,2 – bis (4 – chlorophenyl) ethane

DDT is very useful in killing disease-carrying insects, especially those responsible for typhus and malaria.

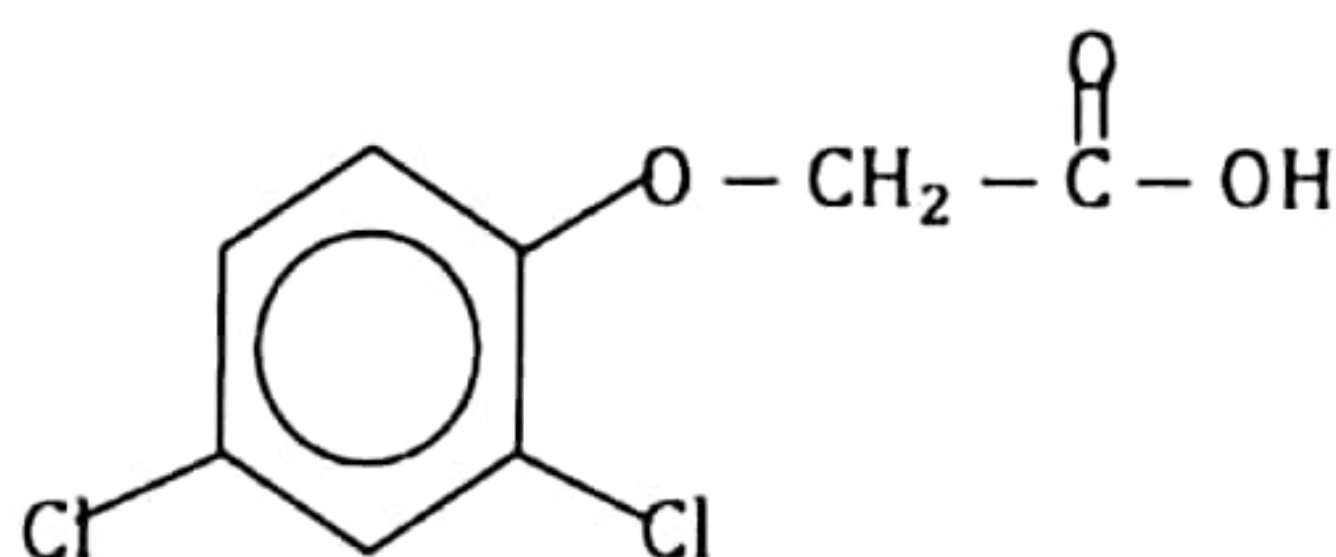
However:

- DDT is very stable and is only slowly broken down in the environment. In other word, DDT is termed to be **non – biogredable** (cannot be easily decompose by living organism).
- Also DDT is fat soluble and is commonly accumulated in the fatty tissue of animals living in the environment where it is exposed. It is said to cause the problem of **biomagnification** (the process by which the concentration of toxic substance increase in each successive link in the food chain).

The above two facts makes DDT to be serious environment pollutant.

On other hand, **herbicides** are substances used for killing weeds.

- For a substance (compound) to act as a good herbicide, it should kill weeds without killing useful plants and crops.
- The use of halohydrocarbons mainly 2,4 – D as herbicide replaced the use of common salt (NaCl) which was not selective as it was killing both weeds and plants as well.
- The structure of 2, 4 – D which very common herbicide is shown below.



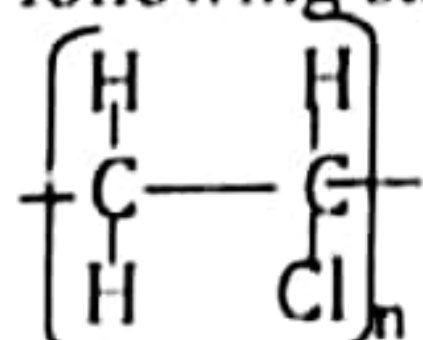
Common name: 2, 4 – Dichlorophenoxyacetic acid (2, 4 – D)

IUPAC name: (2, 4 – dichlorophenoxy) ethanoic acid

iii) Polymers

Halohydrocarbons, particularly vinyl chloride ($\text{CH}_2 = \text{CH} - \text{Cl}$) are very useful in synthesizing polymers.

- Vinyl chloride is used to make polyvinyl chloride (PVC) which is very useful plastic. PVC is commonly used in plumbing, electrical cable insulation, inflatable products (plastic that is capable of being filled with air) and other applications in which it replaces rubber.
- PVC has the following structure.

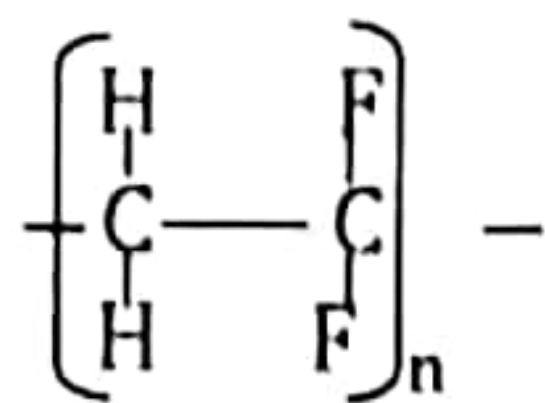


Common name: polyvinylchloride (PVC)

IUPAC name: poly (1-chloroethene)

Another important polymer which can be synthesized from halohydrocarbons is polyvinylidene fluoride or polyvinylidene difluoride (PVDF)

- The polymer is made from 1,1 – difluoroethene ($\text{CH}_2 = \text{CF}_2$) and its structure is shown below:



Common name: polyvinylidenedifluoride (PVDF) or polyvinylidene fluoride

IUPAC name: poly(1,1 – difluoroethene)

iv) Refrigerants and propellants

CFCs are chlorofluorocarbons with the following properties:

- Have low boiling point(they are volatile)
- They are highly unreactive
- They are non-toxic
- They are non-flammable
- They are non-corrosive

The above properties made CFCs (chlorofluorocarbons) to have many uses including the following

- They were useful as refrigerants used in freezers refrigerators and air conditioners
- They were used as blowing agents to produce packaging material and foam.
- They were used as cleaning fluids for printed computer circuits and other electronic device
- They were used as propellants in aerosol sprays.

The reader may wonder why there is 'they were' 'they were' everywhere on the uses of CFCs! *What a thing made CFCs unworthy in today world?* Don't worry, here is the reason!

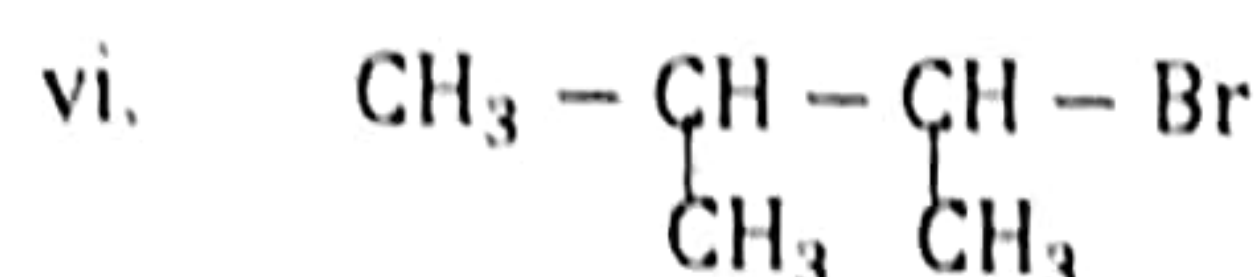
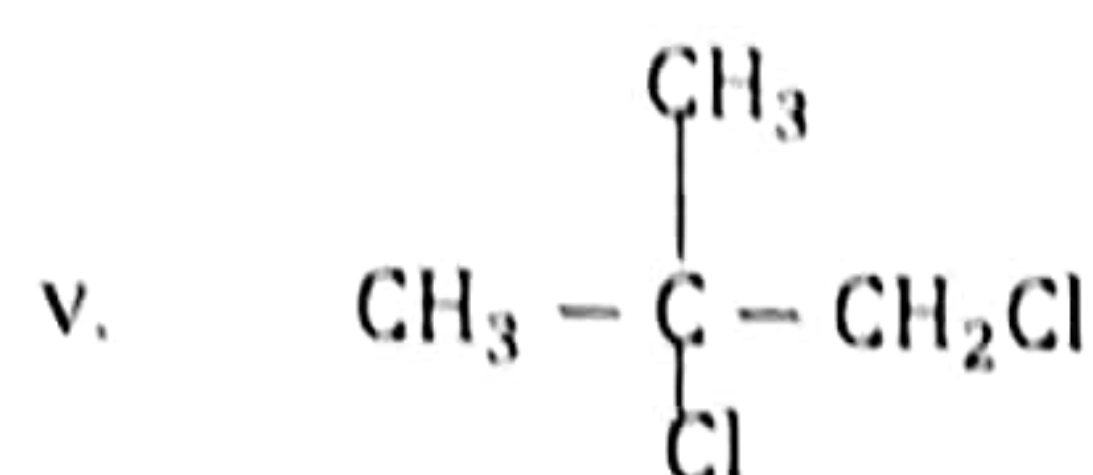
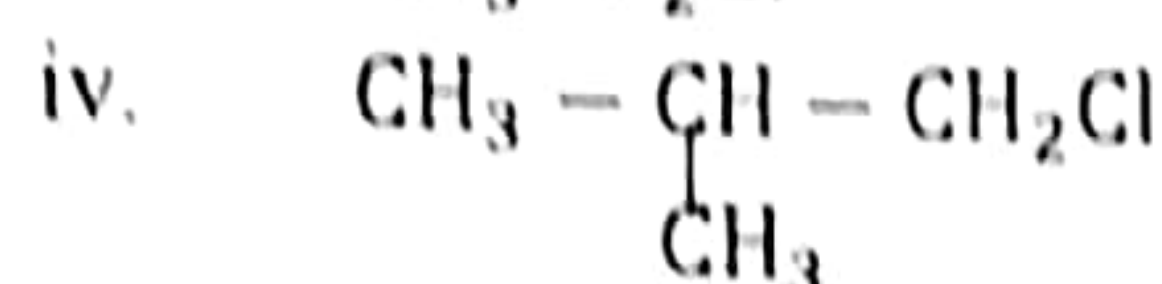
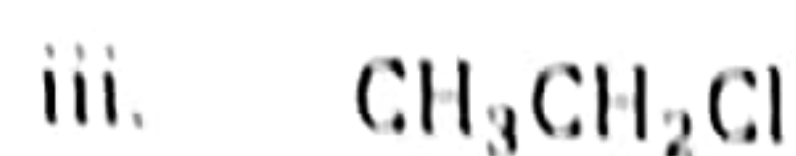
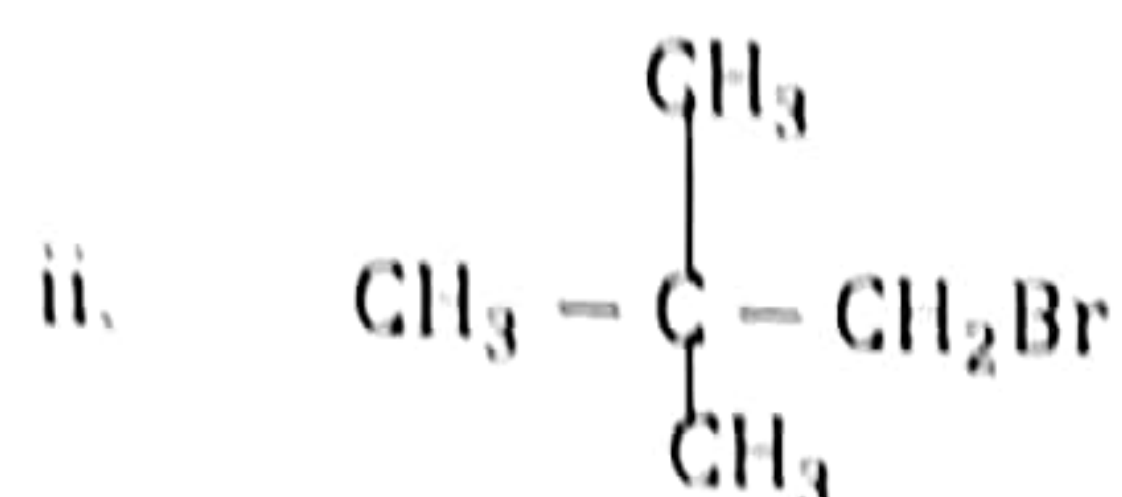
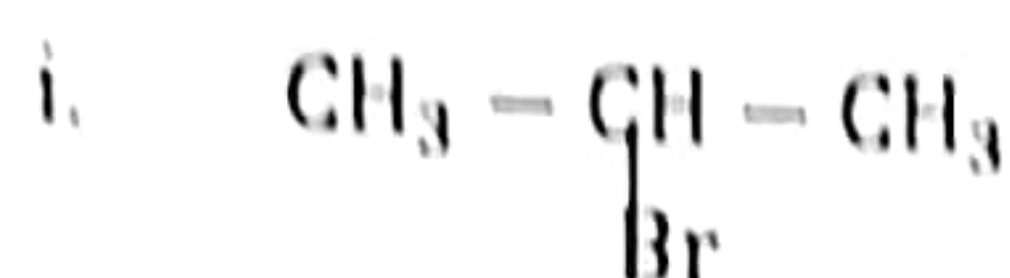
Since CFCs are unreactive and very stable. And since they are volatile they can manage to travel safely in the lower atmosphere up to upper atmosphere (stratosphere) where they meet with highly energetic ultra-violet radiation which is able to break $\text{C} - \text{Cl}$ bond to produce chlorine radicals.

- These radicals initiate chain reactions that lead to the destruction of ozone(O_3) thus causing ozone layer depletion (the matter is deeply discussed in the book titled '**Environmental and soil chemistry**' in the Ngaiza's series of Advanced Chemistry). For this reason CFCs are no longer produced for such uses.

PRACTICE EXERCISE 17

Problem 1

Classify the following haloalkanes as primary, secondary or tertiary.



Problem 2

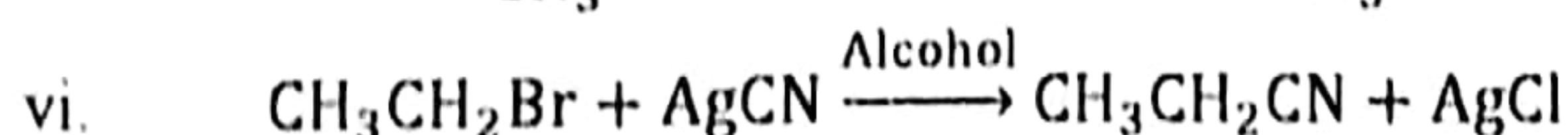
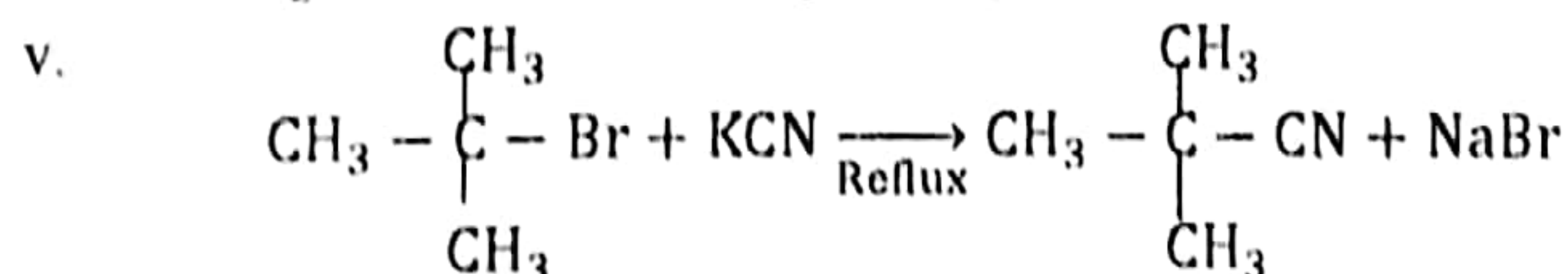
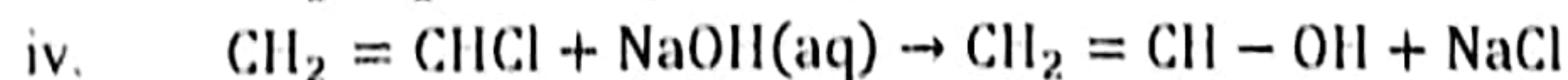
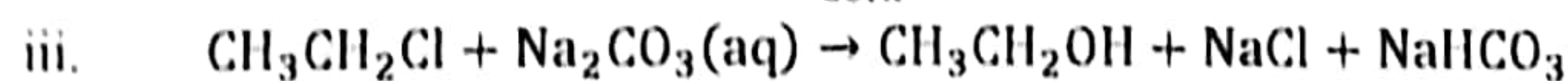
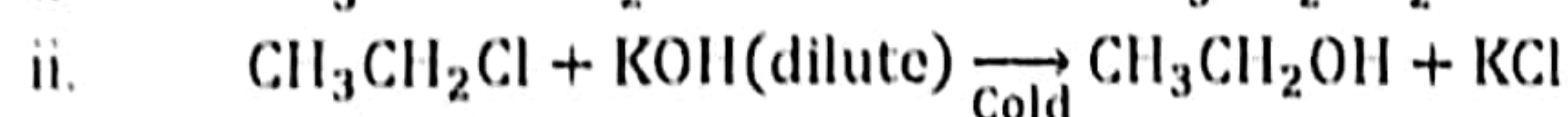
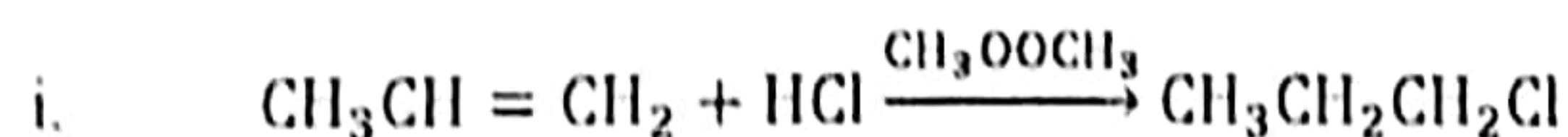
By indicating clearly conditions for reactions write equation to show preparation of 1-bromopropane from the following starting reagents:

i. Propene

ii. Propanol

Problem 3

By giving clear reason(s) say whether the product indicated by each of the following reaction equations is valid or not.



Problem 4

Is the conversion of propane into 1-bromopropane single step or multi-step? Explain your choice and show how the conversion is carried out.

Problem 5

Complete the following organic reactions:

- i.
$$\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{Br} + \text{CH}_3\text{C} \equiv \text{CNa} \rightarrow$$
- ii. $\text{CH}_3\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{SNa} \rightarrow$
- iii. $2\text{CH}_3\text{CH}_2\text{Br} + \text{Ag}_2\text{O} \xrightarrow{\Delta}$
- iv. $\text{Br} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - \text{Br} + 2\text{Na} \xrightarrow[\Delta]{\text{Dry ether}}$
- v. $\text{C}_6\text{H}_5\text{Cl} + \text{NaOH(aq)} \xrightarrow{25^\circ\text{C}}$

Problem 6

List down at least three uses and three hazards of halohydrocarbons

Problem 7

Write down chemical equations to show formation of:

- i. Gilman reagent
- ii. Grignard reagent
- iii. Diphenyl by using Ullmann reaction
- iv. Frankland reagent
- v. Cyclic propane by Freund reaction

Chapter 18

ALCOHOL AND PHENOL

These are organic compounds with hydroxyl (OH) group as functional group.

- Alcohols and phenol are formed when at least one hydrogen atom of hydrocarbons is replaced by hydroxyl group.
- When the hydrogen atom is replaced from aliphatic hydrocarbon the resulting compound is known as an **alcohol**.
- When the hydrogen atom is replaced from benzene then the resulting compound is known as **phenol** (also known as **carbolic acids**).
- Most of properties of alcohol resemble with those of phenol due to similarity in their functional group but some properties are different due to difference in their structure.

CLASSIFICATION OF ALCOHOLS

(Like haloalkanes) According to number of alkyl groups which are directly bonded to a carbon with OH alcohols can be classified into three categories.

- Primary (1°) alcohols
- Secondary (2°) alcohols
- Tertiary (3°) alcohols

Primary (1°) alcohols

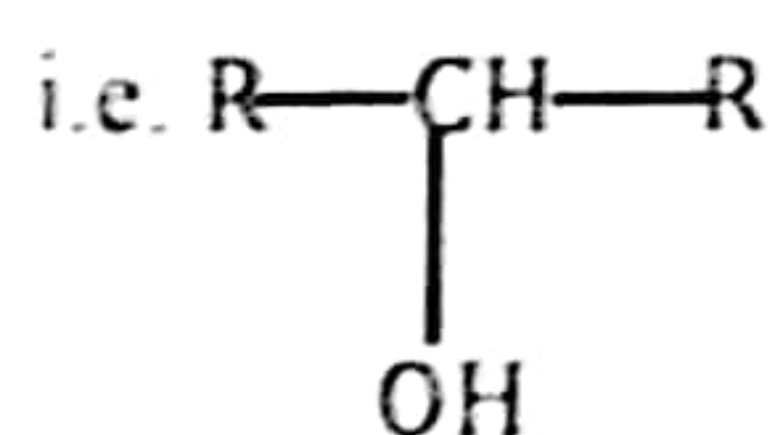
These are alcohols whereby a carbon with hydroxyl group is also directly bonded to one alkyl group only.

Thus for alcohols with one hydroxyl group, the carbon with OH is also directly bonded to two hydrogen atoms i.e. RCH_2OH

Secondary (2°) alcohols

These are alcohols whereby a carbon with hydroxyl group is also directly bonded to two alkyl groups.

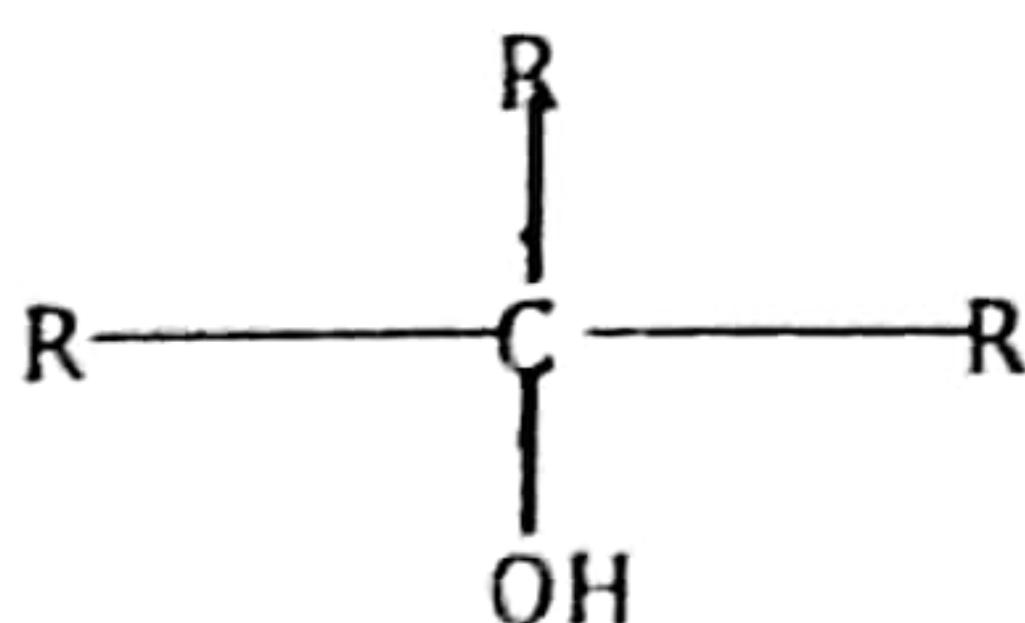
Thus for alcohol with one hydroxyl group, the carbon with OH is also directly bonded to one hydrogen atom only.



Tertiary (3°) alcohols

There are alcohols whereby a carbon with hydroxyl group is also directly bonded to three alkyl groups

Thus there is no hydrogen which is directly bonded to the carbon with OH.



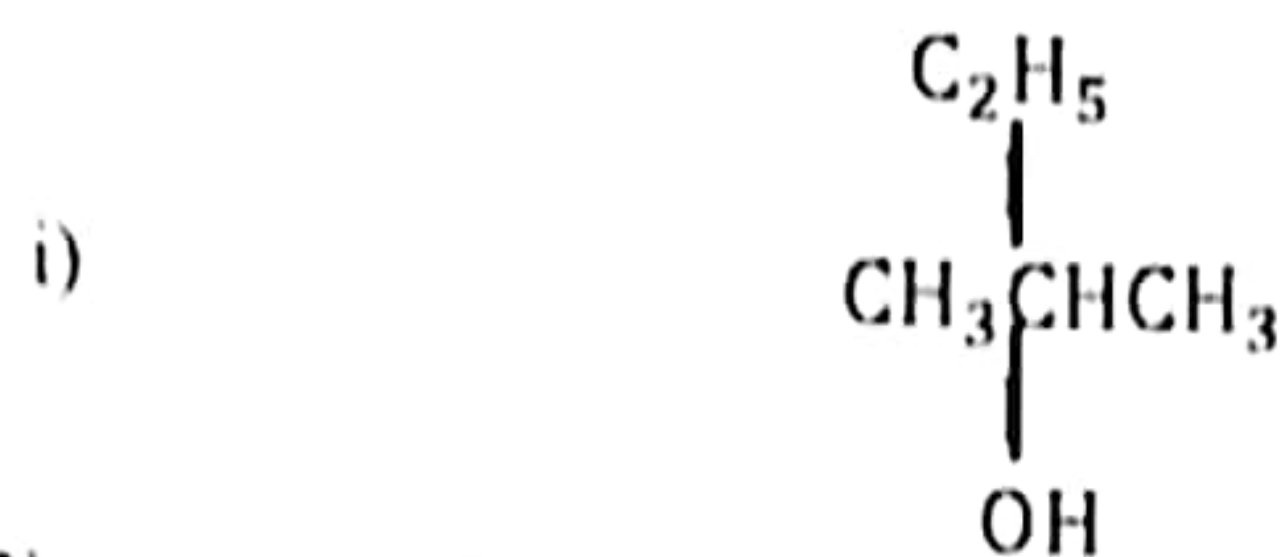
NOMENCLATURE OF ALCOHOLS

Rules of naming alcohols are the same as those of alkanes with the following modifications:

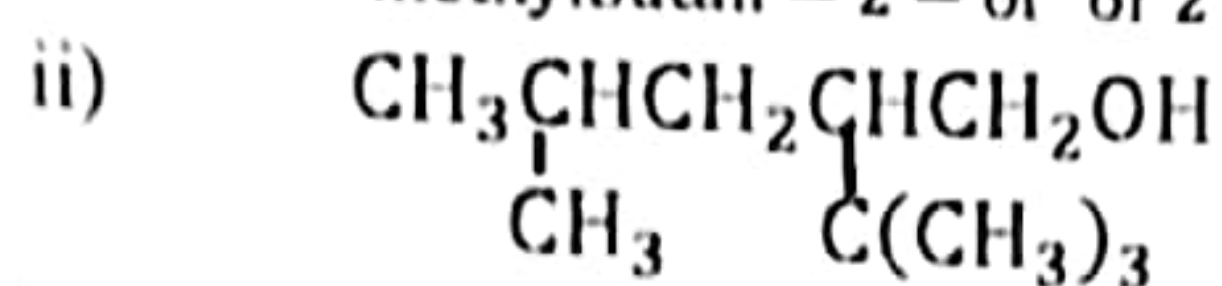
- The parent chain must contain hydroxyl group (OH)
- Numbering carbons starts at the end closer by hydroxyl group
- Position of hydroxyl group should be indicated by using Arabic numerals.
- In giving a parent name of alcohol, the name must end with suffix -ol (after leaving a letter 'e' from corresponding name of the hydrocarbon)

Example 1

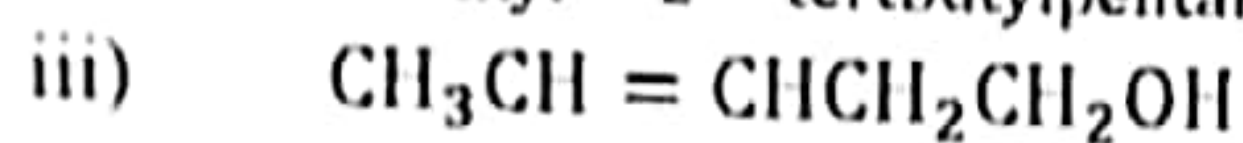
Give a systematic (IUPAC) name of the following organic compounds.



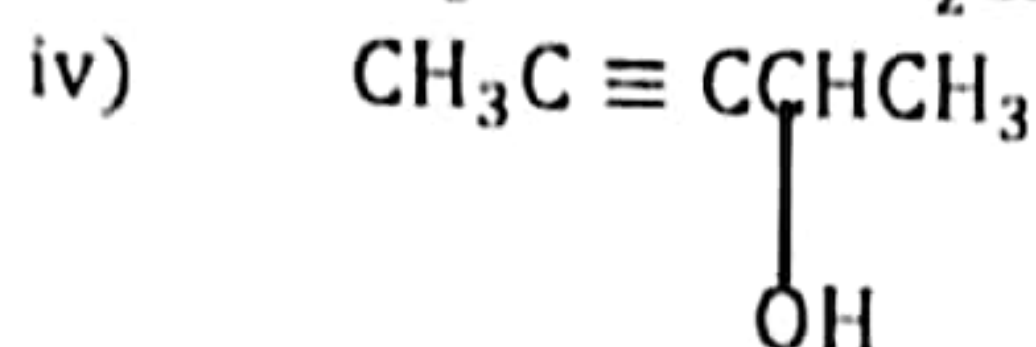
Name: 2 - methylbutan - 2 - ol or 2 - methyl - 2 - butanol



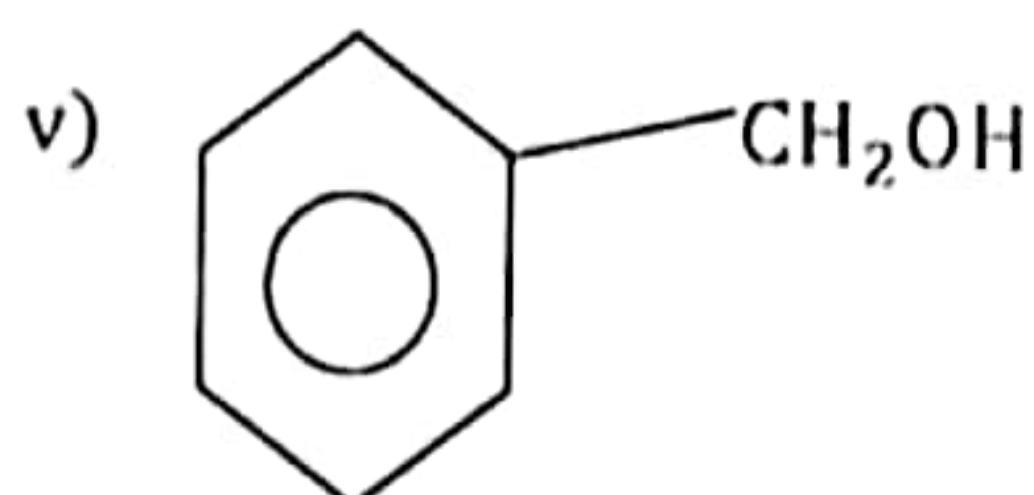
Name: 4 - methyl - 2 - tertbutylpentan - 1 - ol



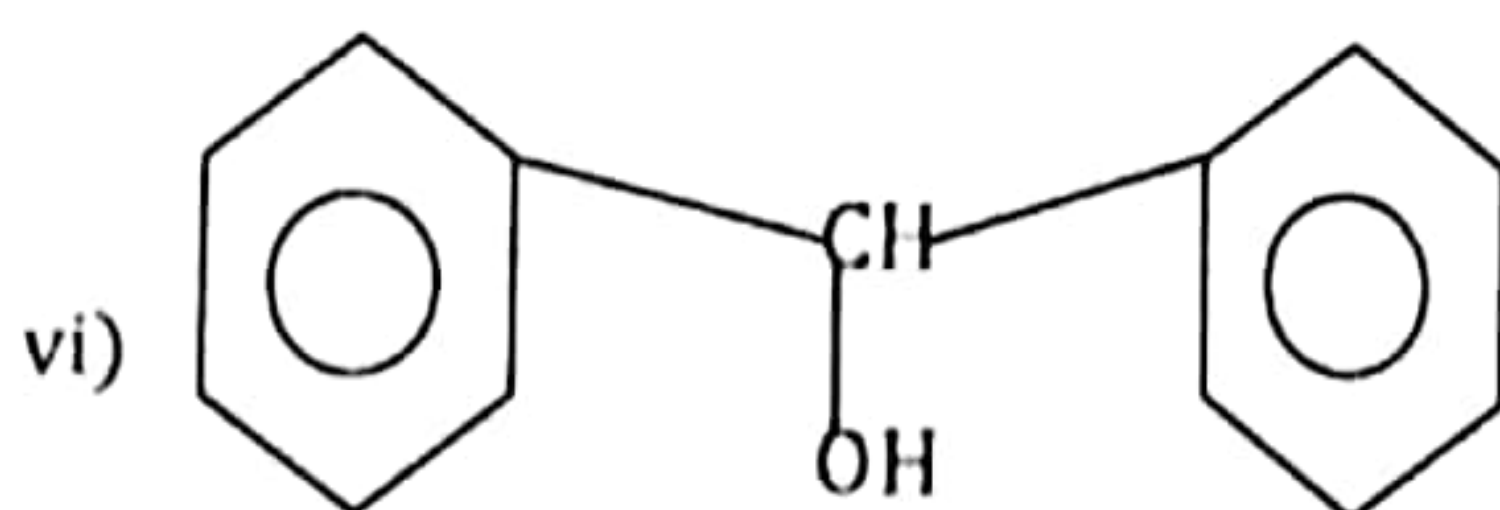
Name: pent - 3 - en - 1 - ol



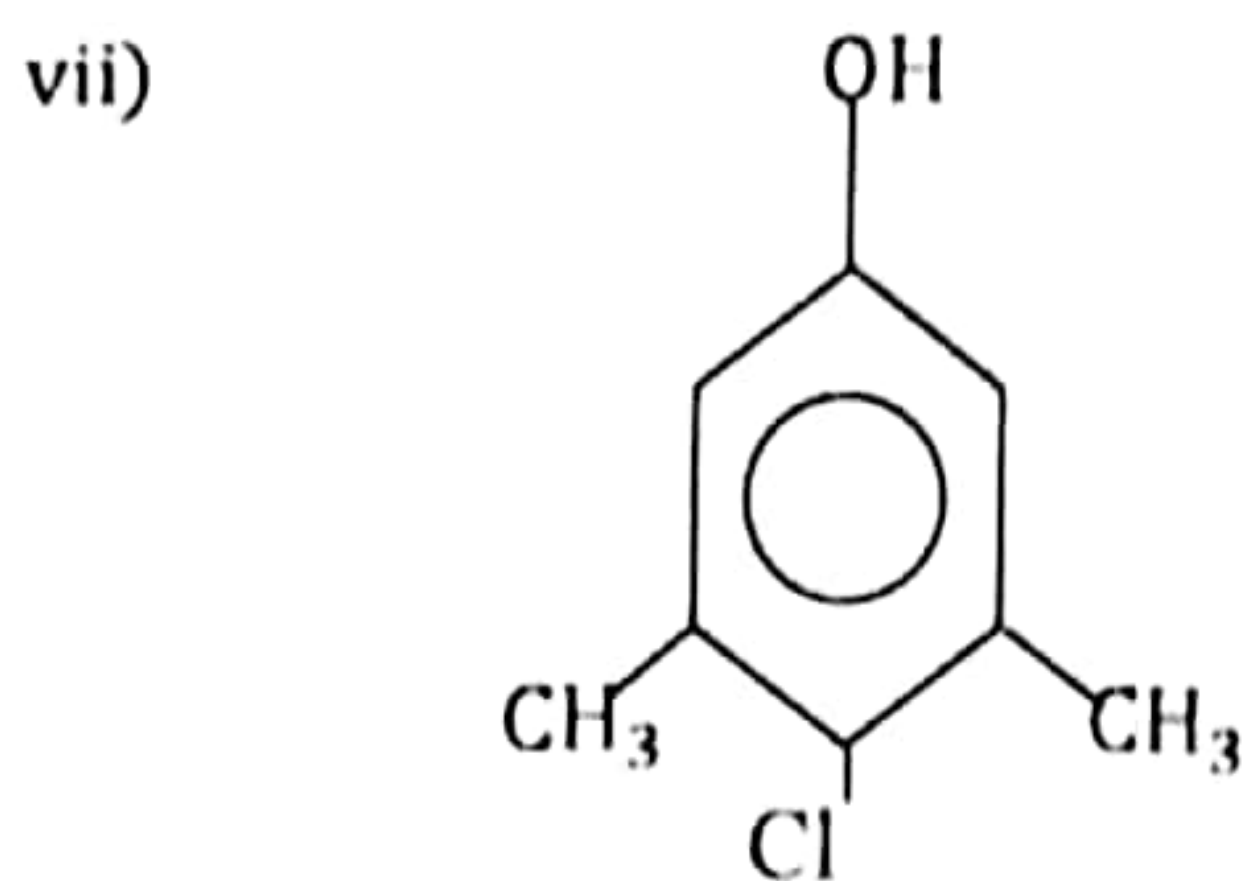
Name: pent - 3 - yn - 2 - ol



Name: 1 - phenylmethanol (common name: benzyl alcohol)

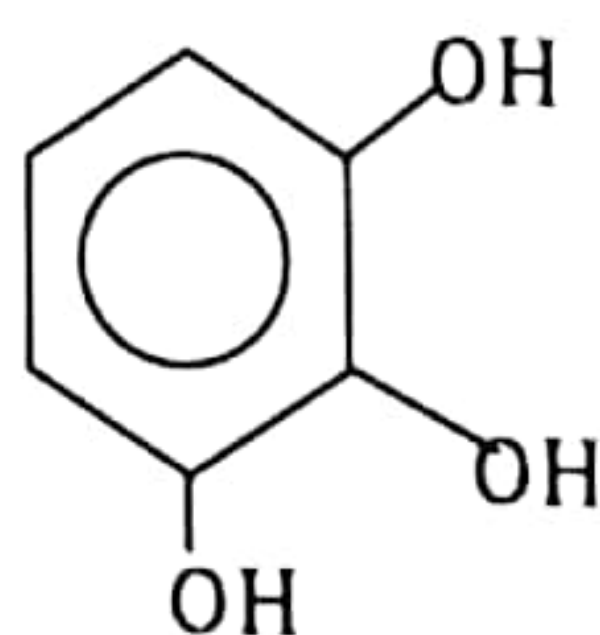


Name: 1,1 - diphenylmethanol



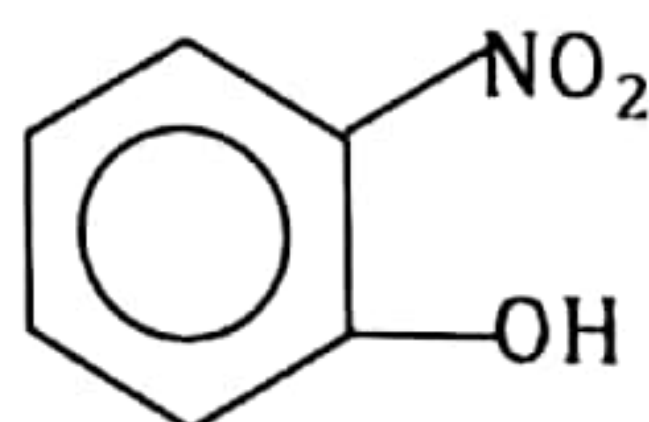
Name: 4 - chloro - 3,5 dimethylphenol (common name: dettol)

viii)



Name: 2, 3 – dihydroxyphenol or 1,2,3 – trihydroxybenzene

ix)



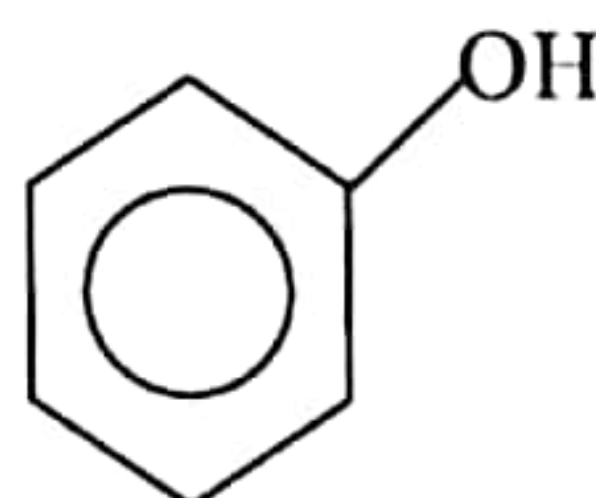
Name: 2 – nitrophenol

x) $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{OH}$ Name: propane – 1,3 – diol

xi) $\text{CH}_2\text{OHCH}=\underset{\text{OH}}{\text{C}}\text{CH}_2\text{OH}$

Name: but – 2 – ene – 1,2,4 – triol

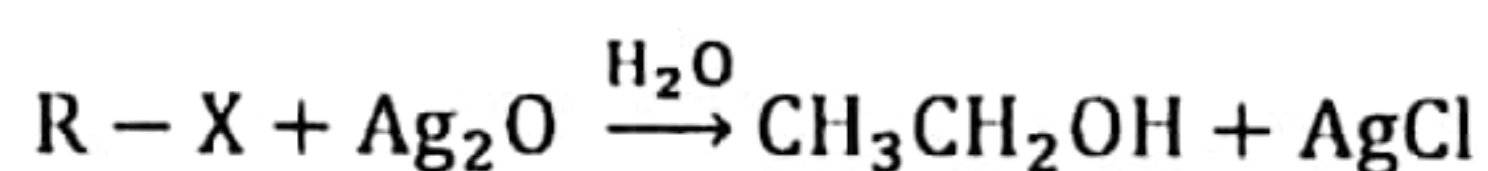
xii)



Name: hydroxybenzene (common name: phenol)

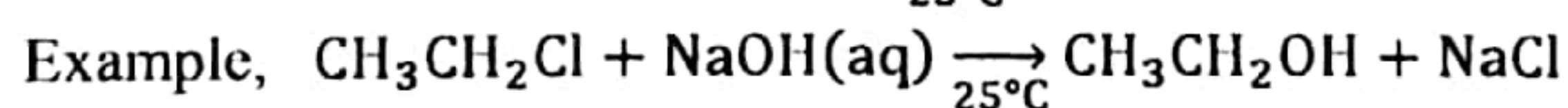
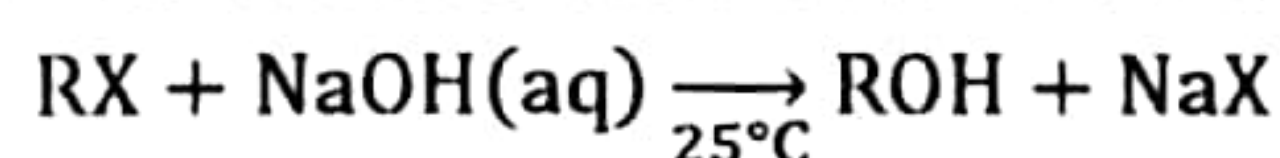
PREPARATION OF ALCOHOLS

a) Reaction between haloalkane and moist silver oxide (silver oxide under presence of water).
Generally;

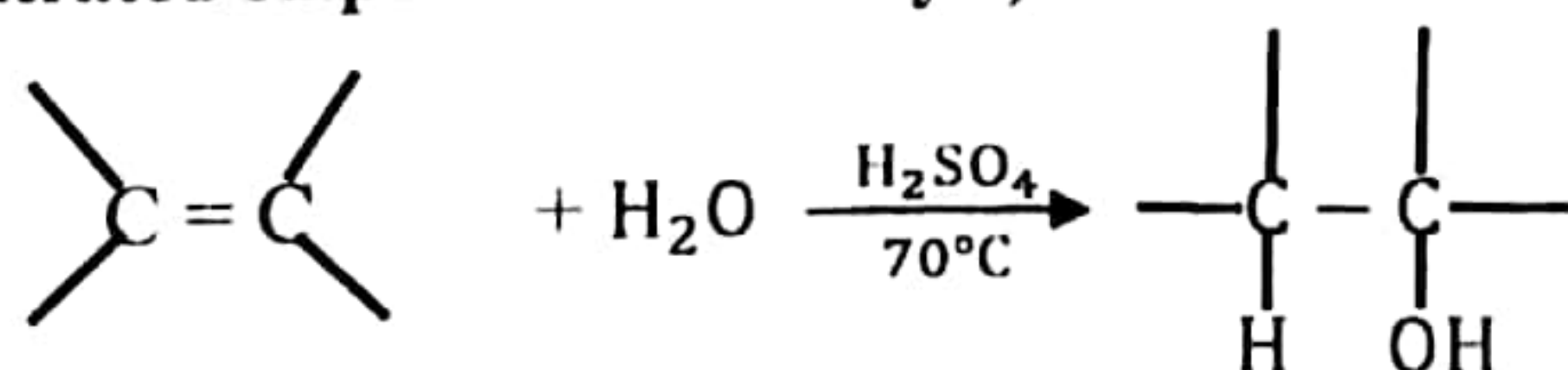


b) Reaction between haloalkane and strong alkaline solution

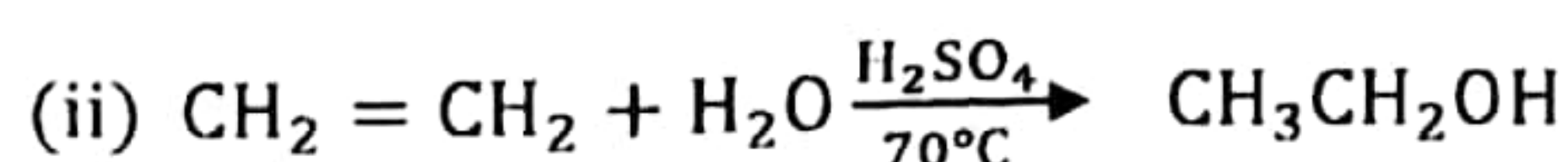
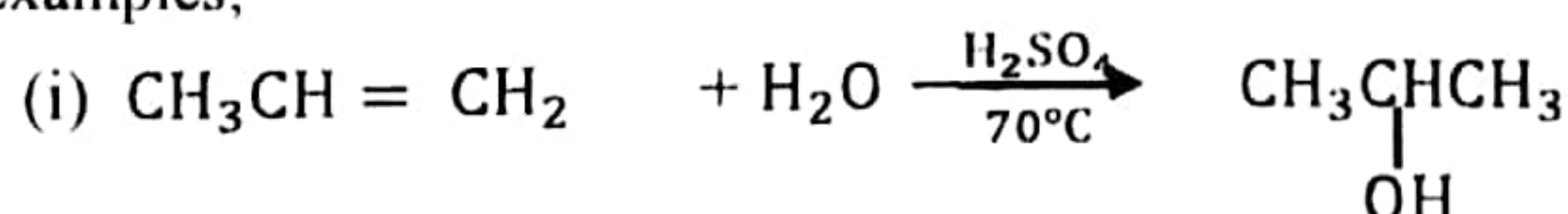
Haloalkane react with alkaline solution like NaOH and KOH yielding alcohol e.g. in case of NaOH;



c) Acidic hydrolysis of alkane (Reaction between alkene and water under presence of concentrated sulphuric acid catalyst).

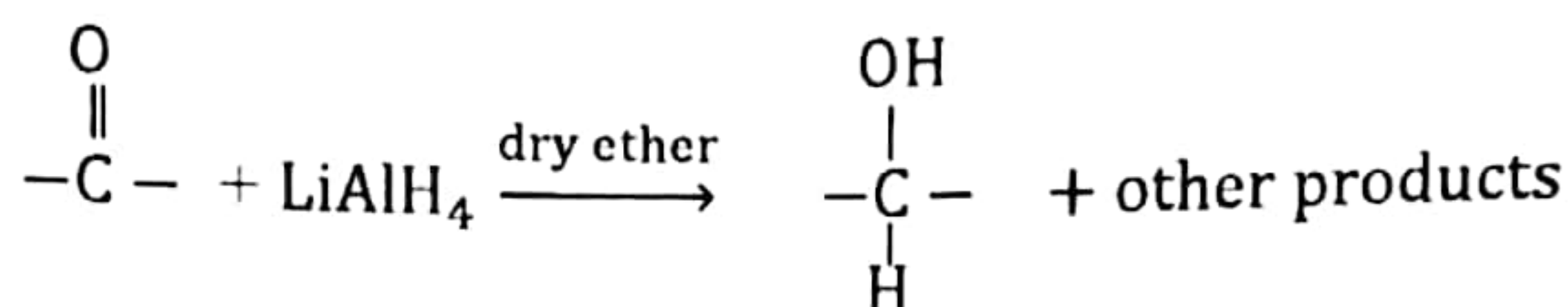


Examples;

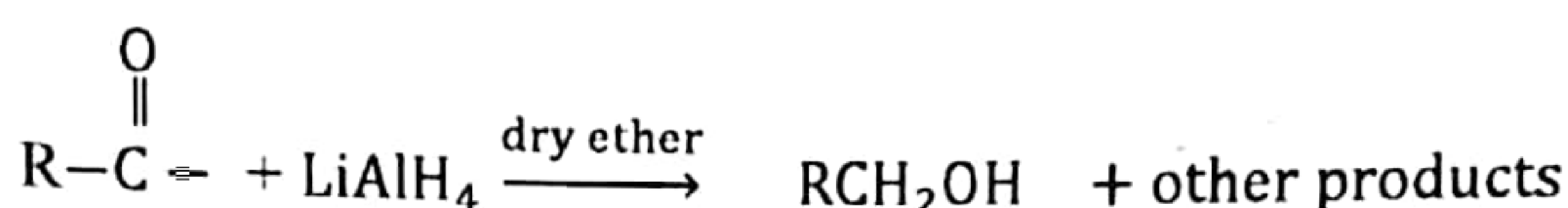


d) Reduction of carbonyl compounds

Carbonyl compounds react with reducing agent like LiAlH_4 , yielding alcohols. Generally;

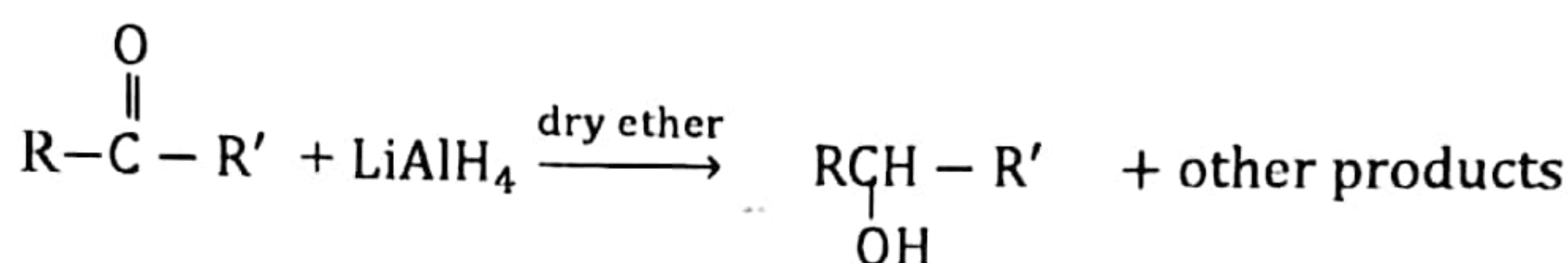


Aldehyde gives primary alcohol
i.e



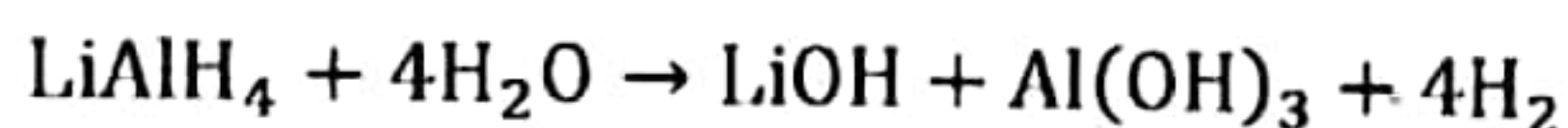
While

Ketone gives secondary alcohol
i.e

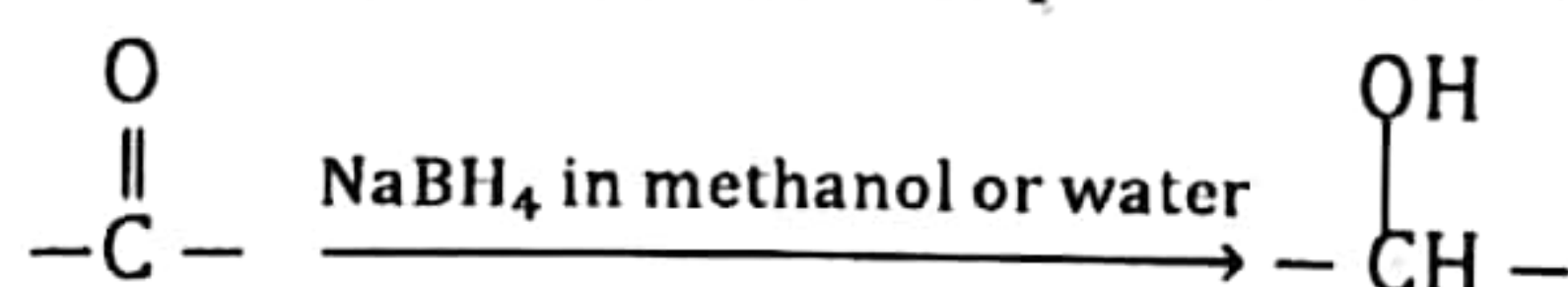


The reduction of carbonyl compound by LiAlH_4 is done in inert solvent like dry ethoxyethane (ether), why?

- This is simply because LiAlH_4 is very powerful reducing agent, it reacts violently with water (even with alcohol!) to evolve hydrogen gas. So the inert solvent, ethoxyethane make the LiAlH_4 less reactive and more selective.

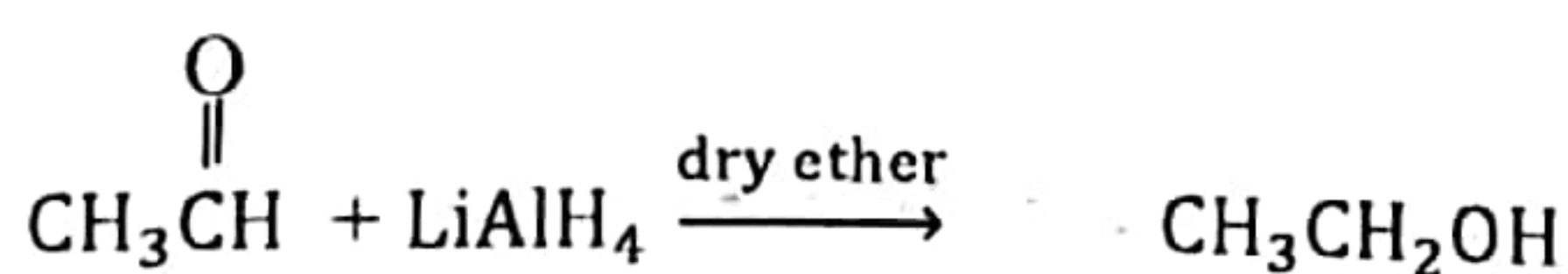


Also less powered reducing agent, NaBH_4 can also be used and it is more appropriate to use this method because it (NaBH_4) can be used in aqueous or methanolic solution.

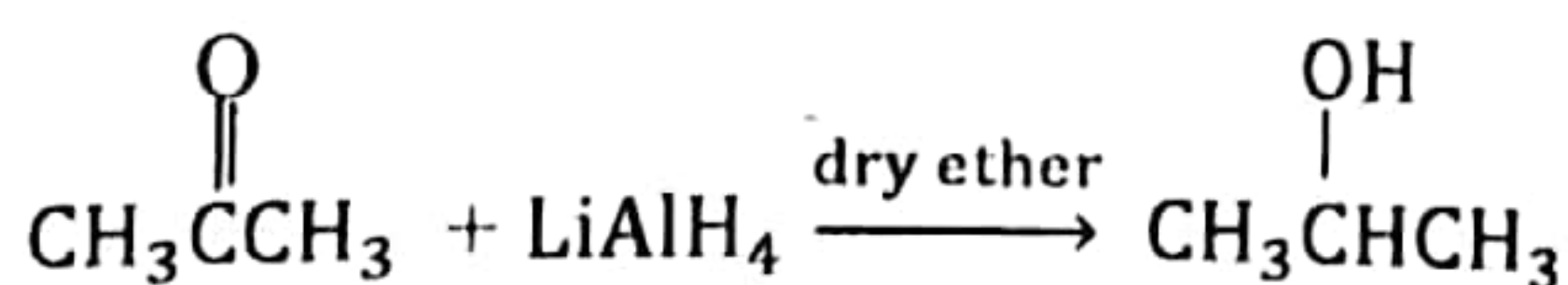


Examples;

i)



ii)

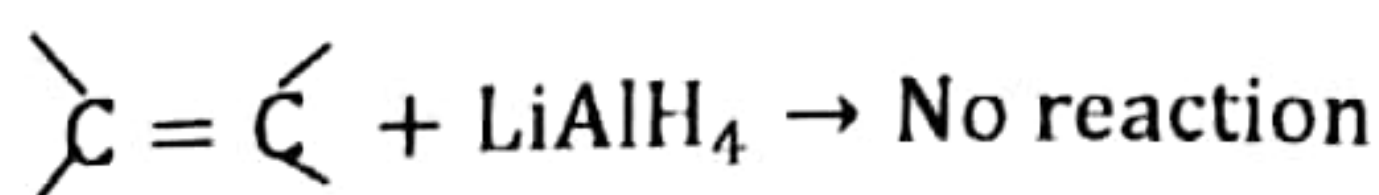


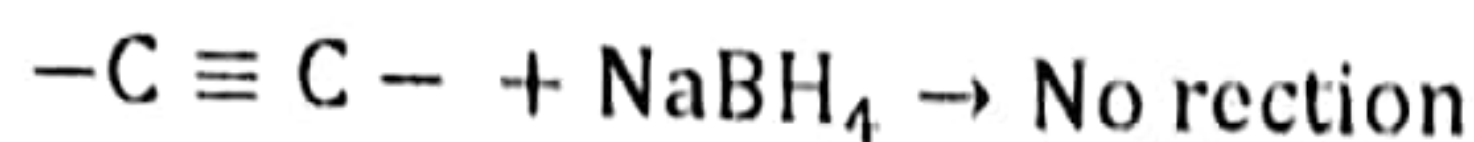
Little challenge!

Although LiAlH_4 and NaBH_4 are reducing agents (they add hydrogens to the compounds) they can never be used to reduce alkene (or alkyne) to alkane, why?

- This is simply because the attacking species in LiAlH_4 and NaBH_4 are nucleophilic. Therefore the negative hydride ion in AlH_4^- and BH_4^- are strongly repelled by high electron density in $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ which contain nucleophilic pi bond too and hence the reaction will not occur.

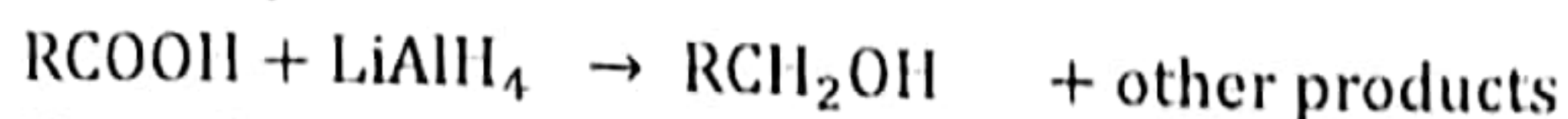
That is:





e) Reduction of carboxylic acid

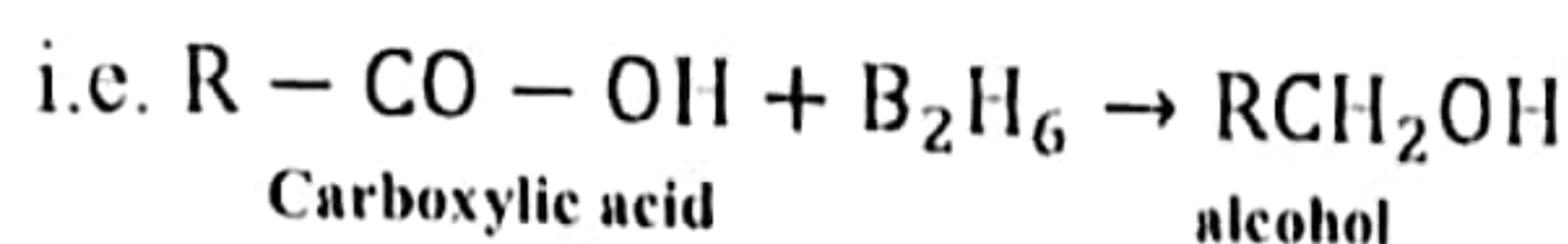
Carboxylic acid reacts with strong reducing agent like LiAlH_4 yielding primary alcohols
Generally:



Example,

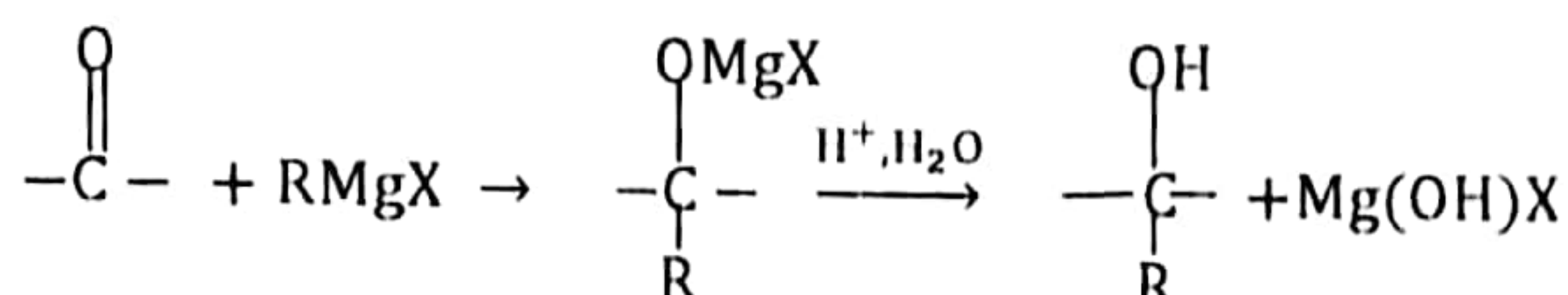


Diborane, B_2H_6 can also be used to reduce carboxylic acid to primary alcohol

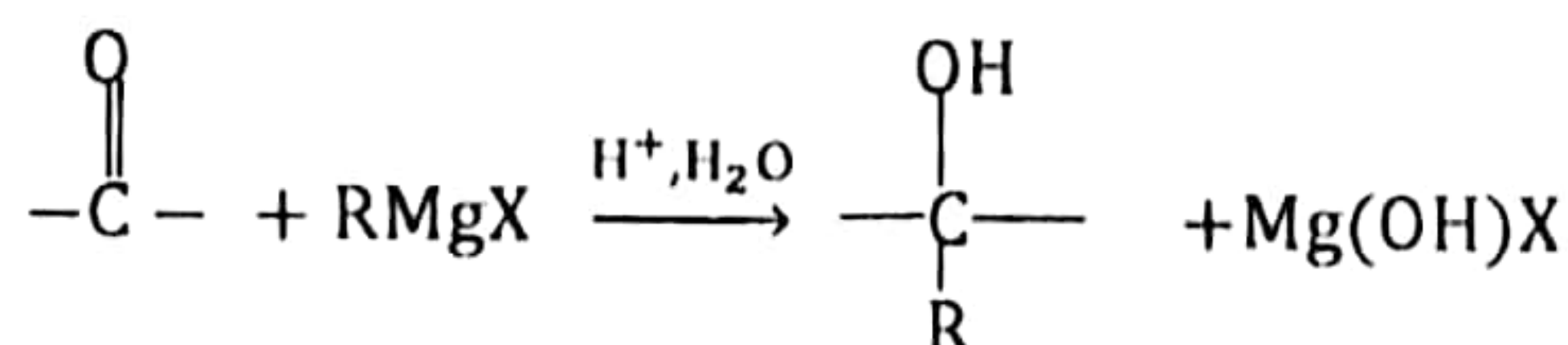


f) Reaction between grignard reagent and carbonyl compound followed by acidic hydrolysis

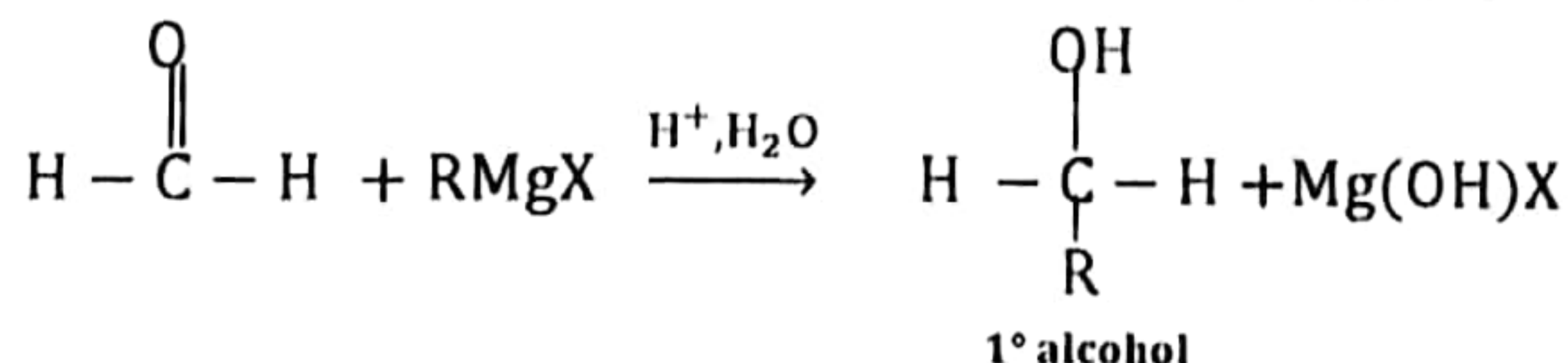
Generally;



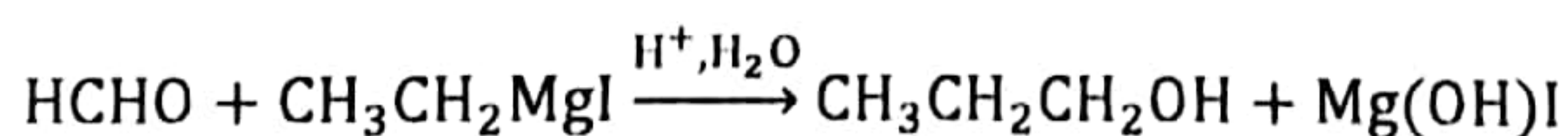
Or



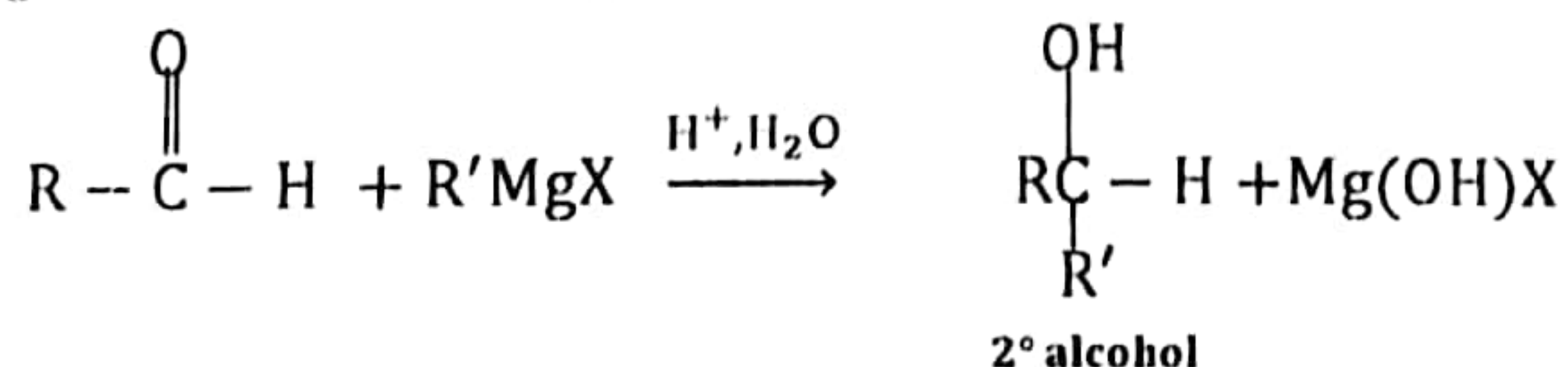
If the aldehyde used is methanal, primary alcohol is formed.



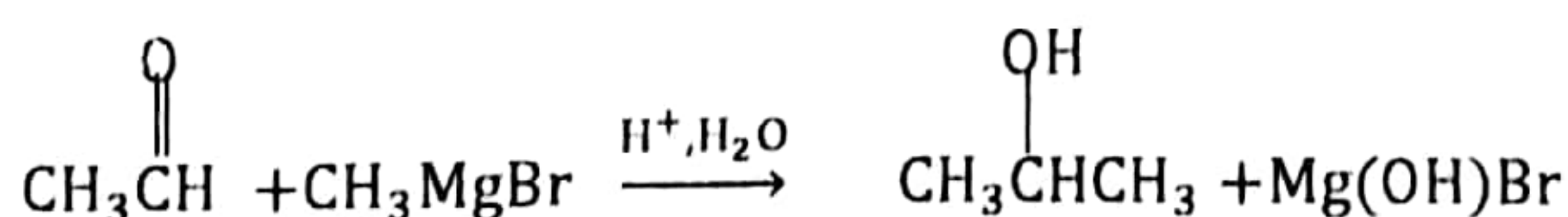
e.g



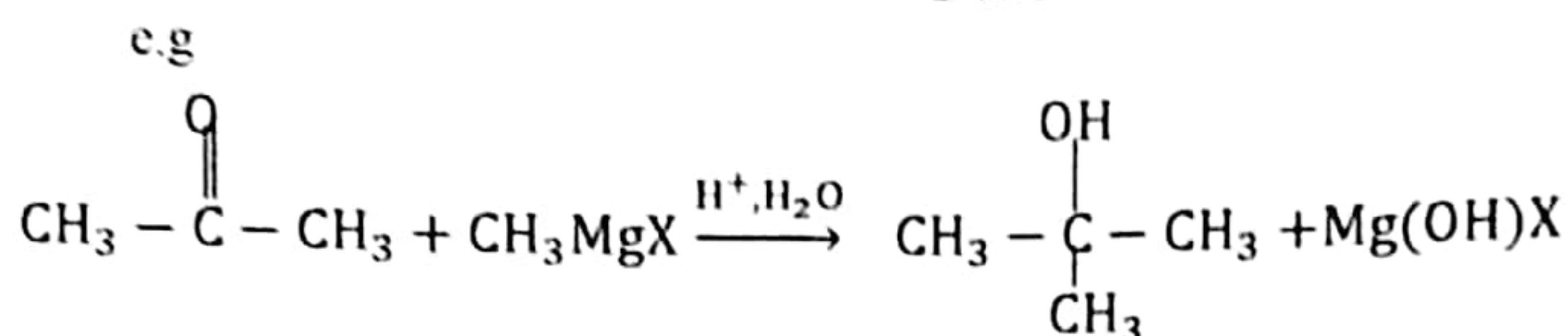
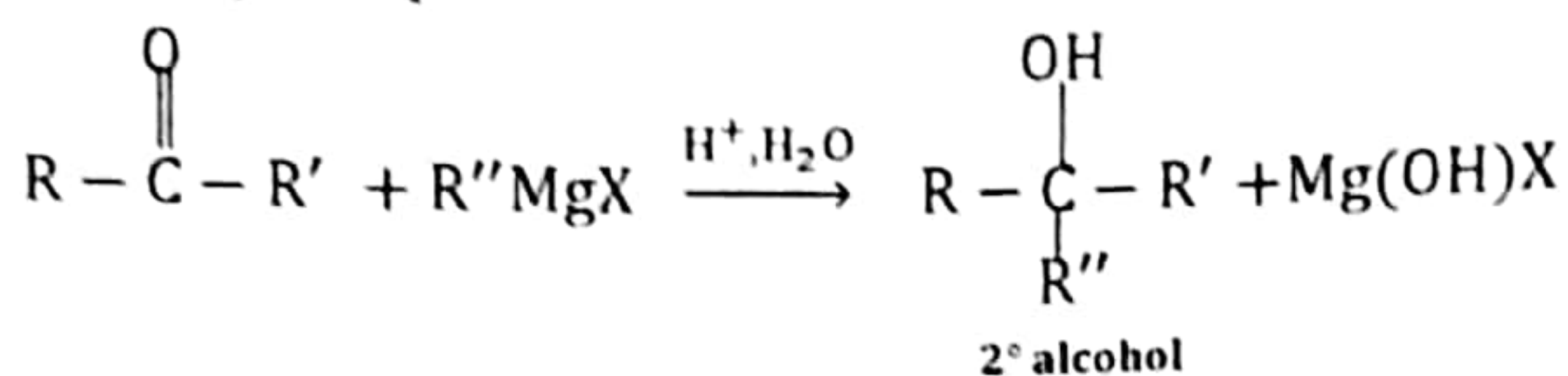
If higher member of aldehyde is used, secondary alcohol is formed.



e.g



If the carbonyl compound which is used is ketone, tertiary alcohol is formed.



PREPARATION OF ALCOHOL BY FERMENTATION

Fermentation is decomposition of organic compounds. It is principle behind industrial manufacture of alcohol (like beer, wine and brandy). Its method which employ biological catalysts called **enzymes** found in **yeast**. The enzymes breakdown sugar molecules into ethanol (of 95% ethanol yield).

Industrially ethanol can be manufactured from fermentation of:

- Starch
- molasses

The reader should understood that:

Glucose is rarely used because it's more expensive.

Fermentation of starch

i. Starchy raw materials

These are wheat, rice, maize, potatoes, barley and cereal.

ii. Conversion of starch into maltose

The conversion of starch into maltose is known as **saccharification**. Its carried out as follows:

Malting

Moist starch is allowed to germinate in dark at 20°C

- The germinated starch is called **malt** and this is heated to (to stop further germination) 60°C.
- It is then crushed and extracted with water. This malt extract contains the enzyme called **diastase**.

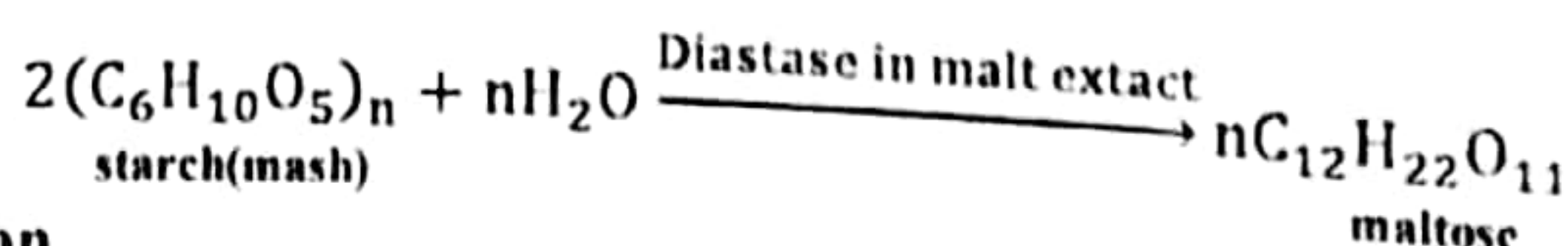
Mashing

To break the cell walls, starch is reacted with superheated steam.

- This exposes the starch inside that forms a paste like mass called **mash**.

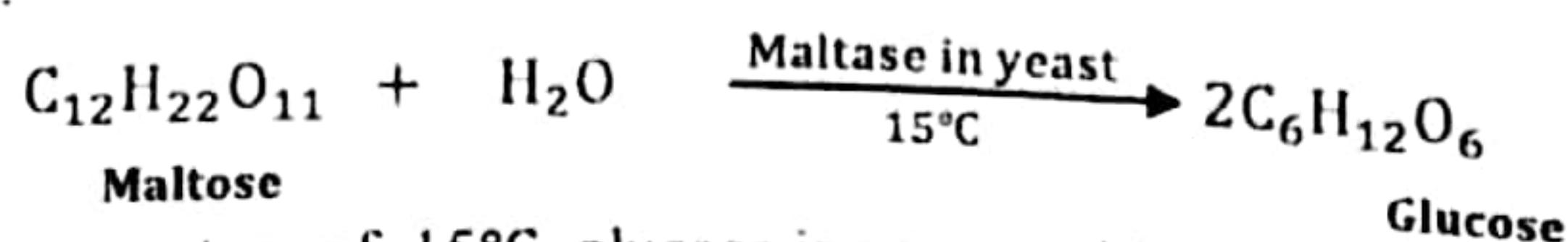
Hydrolysis

On warming with malt extract at 60°C for about half an hour, hydrolysis become complete and maltose is formed.

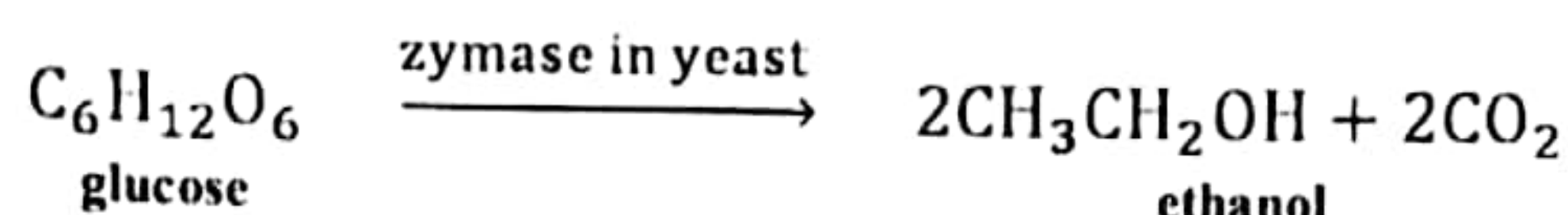


iii. Alcoholic fermentation

On the addition of yeast which contains the enzyme **maltase**, the maltose is broken down into glucose at 15°C.



At maintained temperature of 15°C, glucose is converted into ethanol by the enzyme **zymase**, also found in the yeast



The carbon dioxide obtained as byproduct is recovered and can be sold.

Fermentation of molasses

Molasses is a byproduct of sugar industry which appears as syrup left after separation of cane sugar or beet sugar crystals from concentrated sugar can juice.

- It is a dark coloured syrup mass and contains about of 30% of uncrystallizable sucrose and about 32% of invert sugar (a mixture of glucose and fructose).
- Below are steps in the manufacture of ethanol by fermentation of molasses

(i) Dilution

The molasses is diluted with water until a concentration of 8-10% sugar is obtained in solution.

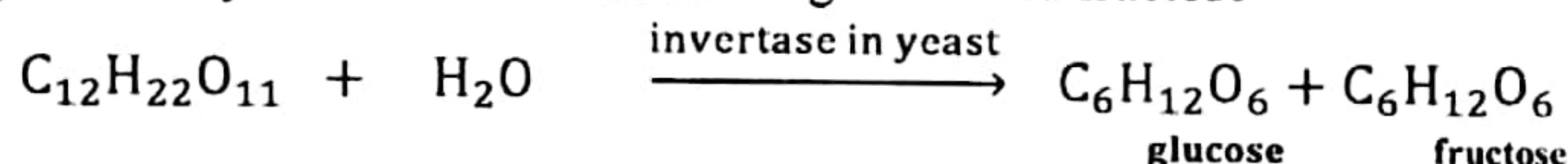
- To discourage bacterial growth, a little sulphuric acid is added to the dilute solution.

(ii) Alcoholic fermentation

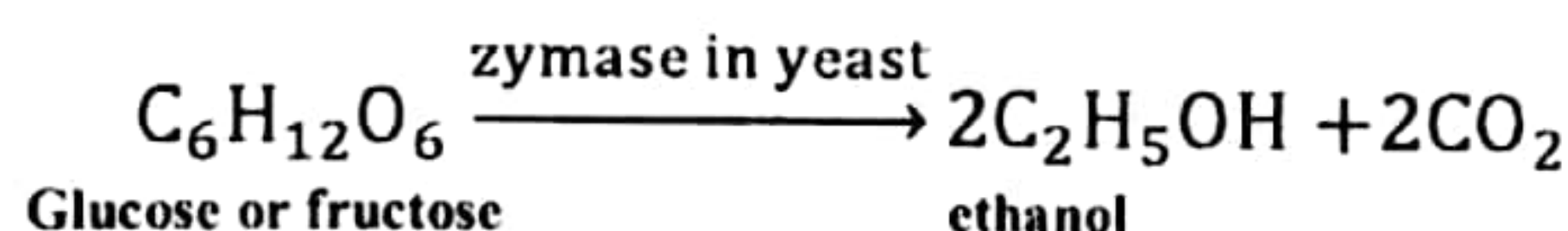
The diluted solution obtained as above is taken in big fermentation tanks and some yeast (5% by volume) is added.

- The temperature is maintained at 60°C and the mixture is allowed to stand for few days.

The enzyme invertase present in yeast converts sucrose into glucose and fructose



The enzyme zymase also present in the yeast, converts glucose and fructose into ethanol and carbondioxide



The fermentation is complete in 3 days

PHYSICAL PROPERTIES OF ALCOHOL

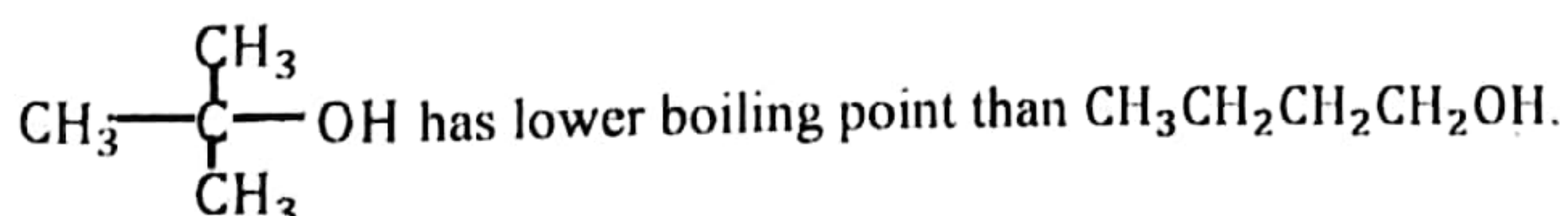
Boiling points of the alcohols increase with an increase of number of carbon atoms (as number of carbon increases the molecular weight also increases).

- This true for alcohols with the same number of hydroxyl groups but differing on the number of carbon atoms which in turn leads to difference in their molecular weight from which the alcohol of great number of carbon atoms also has greater molecular weight. e.g Boiling point of $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is larger than that of $\text{CH}_3\text{CH}_2\text{OH}$

The less branched alcohol has higher boiling point than that of alcohol which is more branched.

- This is true for alcohols with the same molecular weight (also the same number of hydroxyl groups).

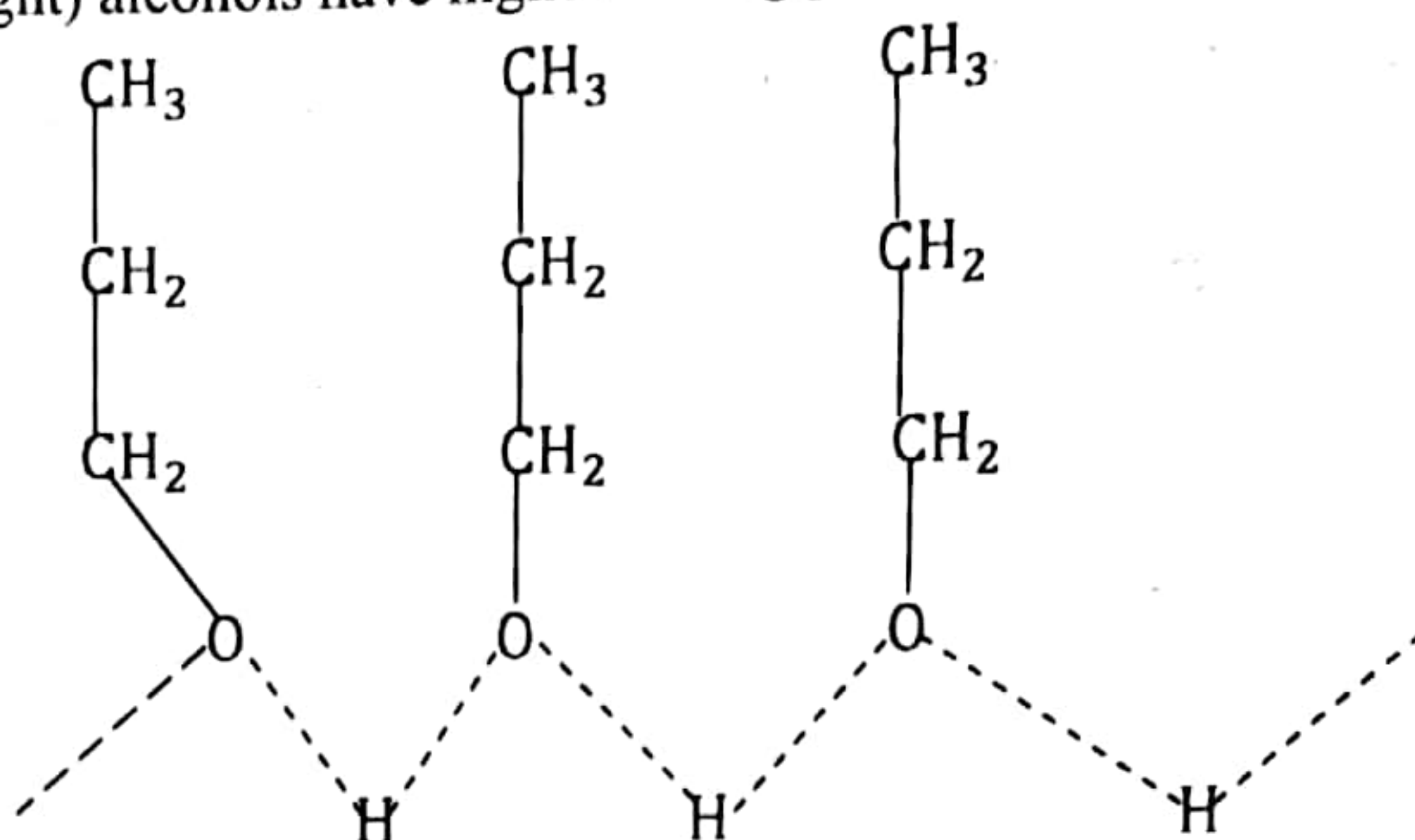
For example;



The more branched has lower boiling point due to the following reasons:

- (i) Poor package of carbon atoms
- (ii) Minimum surface area (branched carbon chain has minimum surface area as it attain more spherical shape and this make Van-der-waals' forces weaker and hence the boiling become easier).

In comparison between alcohols and corresponding member of alkanes (with approximately the same molecular weight) alcohols have higher boiling point due to presence of hydrogen bonding.



For polyhydric alcohol (alcohol with more than one OH group) the boiling point increase with number of hydroxyl groups due to increase in number of positions of making hydrogen bonding.

Example 2

Explain the following: the boiling point of ethyleneglycol is higher among the compound given below although there is little difference in their molecular weight.

Compound	Formula	Molecular weight	Boiling Point in °C
Ethyleneglycol	OHCH ₂ CH ₂ OH	62	197
1 – propanol	CH ₃ CH ₂ CH ₂ OH	60	97
Butane	CH ₃ CH ₂ CH ₂ CH ₃	58	-0.5

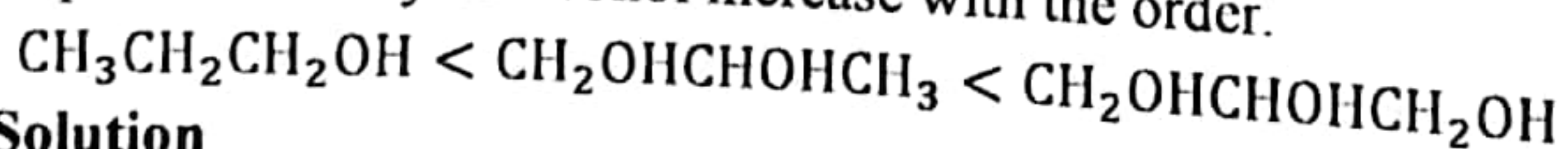
Solution

Boiling point of alcohol increase with an increase in number of OH groups (for polyhydric alcohol) due to increase in number of positions of making hydrogen bonding. Ethyleneglycol has two OH groups so compared to 1 – propanol which has only one OH groups, ethyleneglycol has many positions of making hydrogen bonding and hence its boiling point will be higher. In case of butane, it has no OH group and thus there is no hydrogen bonding at all that is why it has lowest boiling point.

Solubility of alcohol in water decreases with an increase of hydrophobic group (increase in length of carbon chain) due to an increase of non – polar (covalent) character which outweighs (weakens) hydrogen bonding.

Example 3

Explain solubility of alcohol increase with the order.



Solution

For polyhydric alcohol solubility increase with an increase in number of OH groups due to an increase in number of position of making hydrogen bonding that is why solubility of given compounds increase in that order (i.e. the larger the number of OH groups in the alcohol the higher the solubility it becomes).

It should be understood that:

Compared to alcohol, phenol is less soluble in water because lone pair of oxygen in OH group of phenol has been delocalized in mesomerism thus making difficult for phenol to make hydrogen bonding with water.

Alcohol exists as colourless liquid or low melting solid (they always exist as coloured compounds because are easily oxidised by oxygen from air).

Explanation on comparison of acidic strength between alcohols and phenols

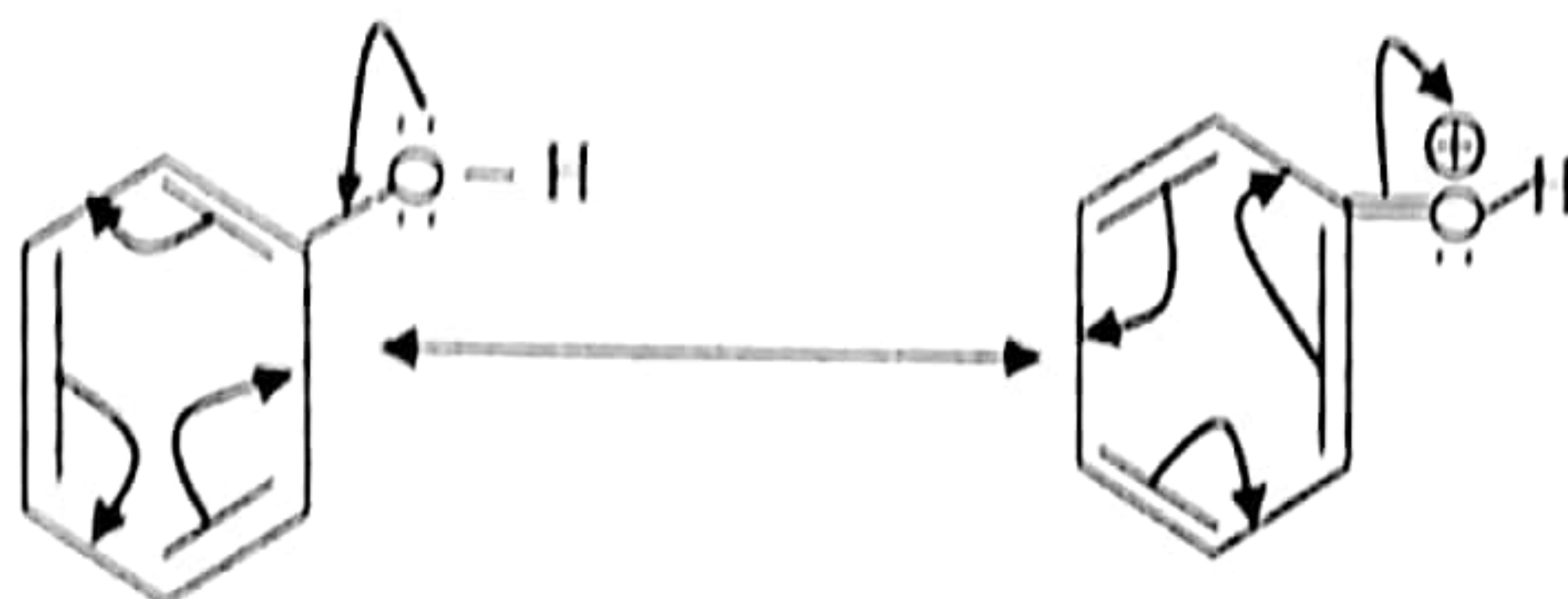
Phenol stronger acid than alcohol due to the following reasons:

- Easiest of releasing hydrogen proton
- Stability of phenoxide ion which is formed after releasing the hydrogen proton

Easiest of releasing hydrogen proton

Lone pair electrons in oxygen of OH group in phenol are not localized; they are involved in mesomerism (+M), that is they are delocalized.

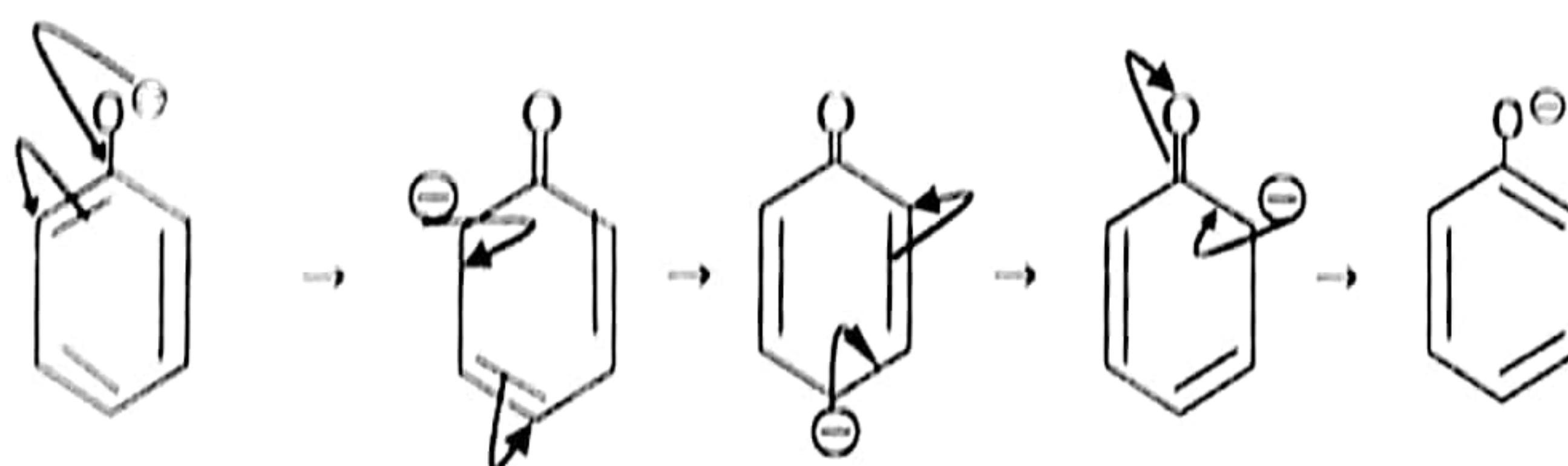
- In the delocalization of lone pair electrons, positive charge in oxygen atom of OH group is formed thus making easier to release hydrogen proton.



There is no such occasion in alcohol

Stability of phenoxide ion which is formed after releasing hydrogen proton

Consider mesomerism of phenoxide ion as shown below



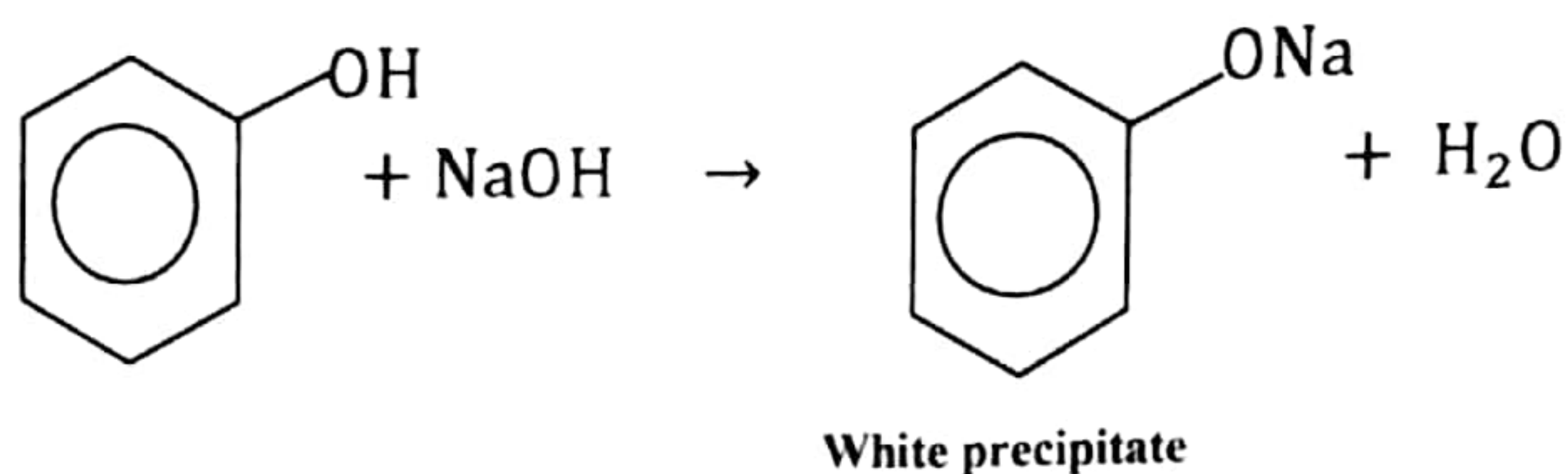
From the above mesomerism, it is clearly understood that negative charged electrons in oxygen atom of phenoxide ion is delocalized thus stabilising the negative charge formed after releasing hydrogen proton (i.e. it can exist on its own without combining with hydrogen proton).

- There is no such occasion in alkoxide ion (RO^-) which is formed in alcohol after releasing hydrogen proton by difficulty.

Chemical reactions which show that phenol is more acidic than alcohols**Reaction with alkaline solution**

Acid react with alkaline solution like NaOH yielding salt and water only.

- Phenol like other acids tends to react with strong alkaline solutions to form phenoxide (salt) and water only. Example; with NaOH phenol yields sodium phenoxide salt and water only.



But,

There is no such reaction with alcohol indicating that alcohol has more basic character and hence phenol is more acidic than alcohol

i.e. Alcohol + Alkane solution $\rightarrow$ No reaction

Note:

The reaction is very important in separating phenol from alcohol because on addition of acidic water like dilute HCl to the phenoxide (appears as residual after filtration), phenol is regenerated.

Question

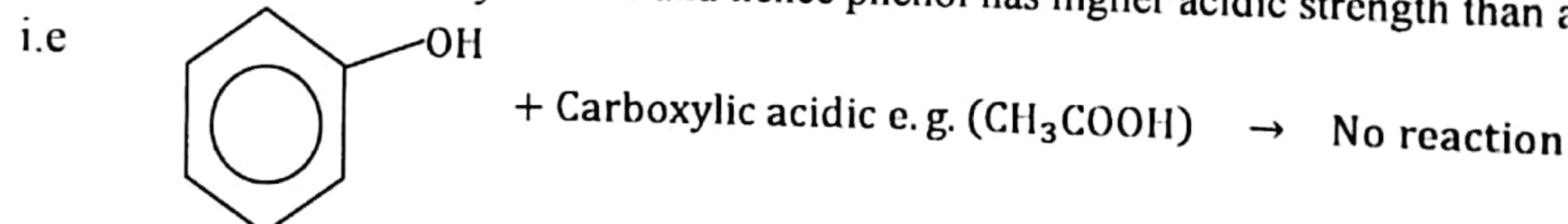
Without using the distillation explain how would you separate the following pair of organic compounds

- (i) Phenol and 1 – hexanol
- (ii) Phenol and benzene

Reaction with carboxylic acid

Alcohols react with carboxylic acid in presence of sulphuric acid to form ester (salt) and water i.e $\text{ROH} + \text{R}'\text{COOH} \rightarrow \text{R}'\text{COOR} + \text{H}_2\text{O}$

– This verify that alcohols has basic character. In case of phenol it does not react with the carboxylic acid either in presence or in absence of sulphuric acid. This verifies that phenol has acidic character like carboxylic acids and hence phenol has higher acidic strength than alcohol.



CHEMICAL REACTIONS OF ALCOHOLS

Chemical reaction of alcohols can be classified into the following categories:

- Reactions which involve replacement of H of OH group.
- Reactions which involve replacement of a whole OH group.
- Reactions which involve OH group and β – hydrogen
- Oxidation

Reactions which involve replacement of hydrogen atom from OH group

(a) Reaction with metals

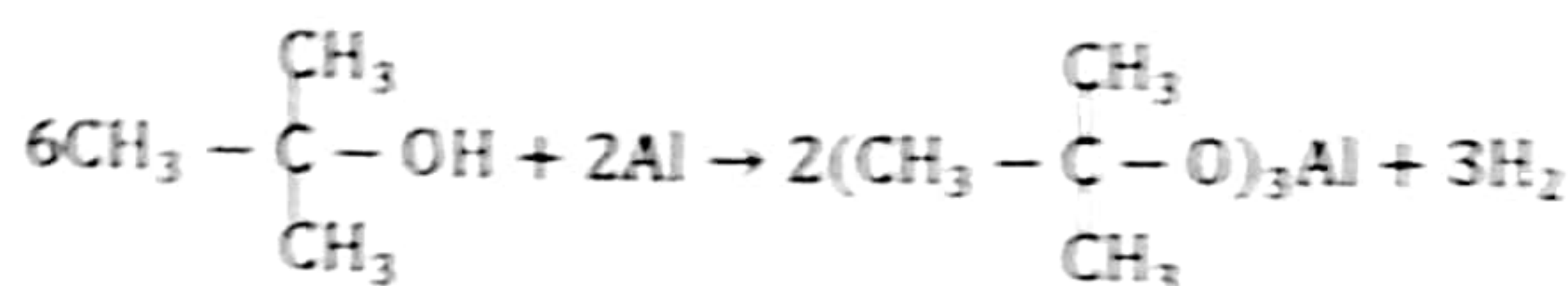
Under this heading, alcohol reacts with strong alkaline metal like Li, Na, and K to form alkoxide and hydrogen gas is evolved.

Generally; $2\text{ROH} + 2\text{M} \rightarrow 2\text{ROM} + \text{H}_2$

M is alkaline metal like Li, Na, K

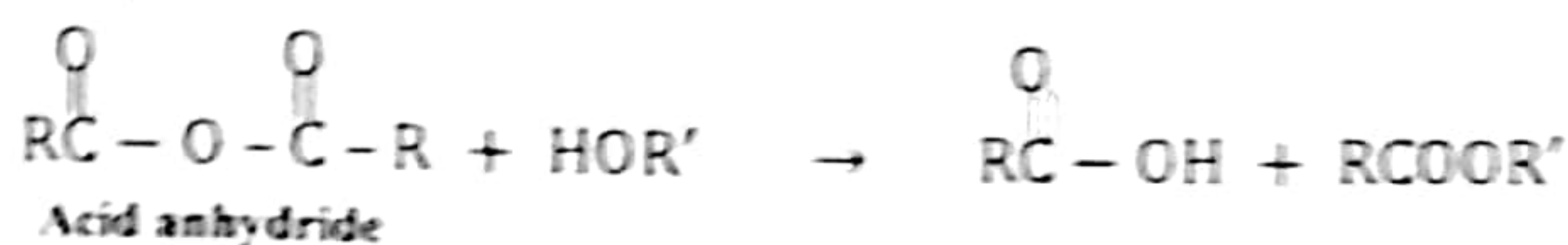
Example: $2\text{CH}_3\text{CH}_2\text{OH} + \text{Li} \rightarrow 2\text{CH}_3\text{CH}_2\text{OLi} + \text{H}_2$
Lithium ethoxide

Similarly,

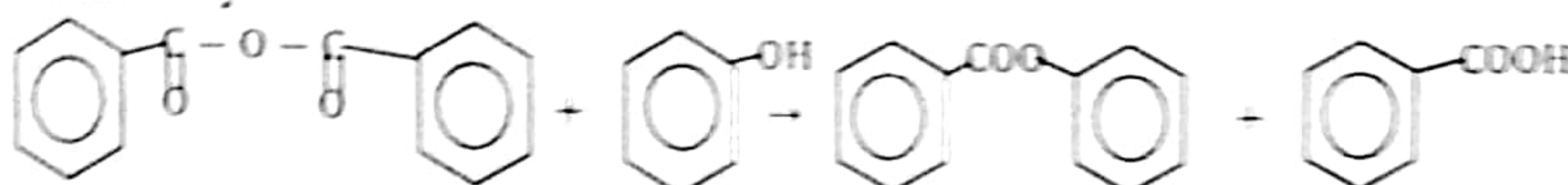


i. Reaction with acid anhydride

Generally



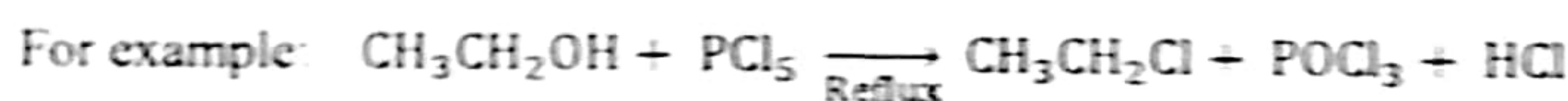
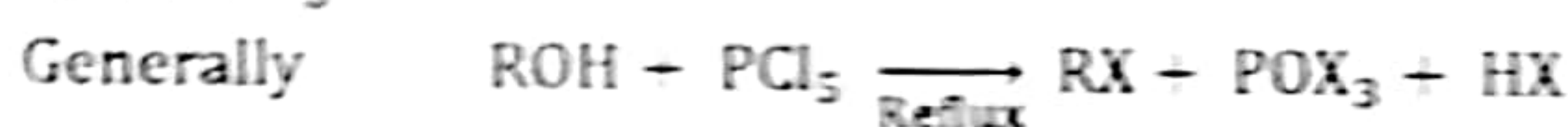
Similarly



Reactions which involve replacement of whole OH group

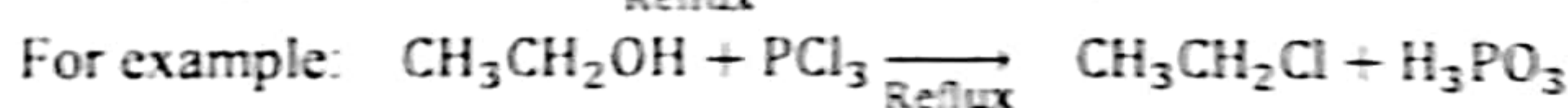
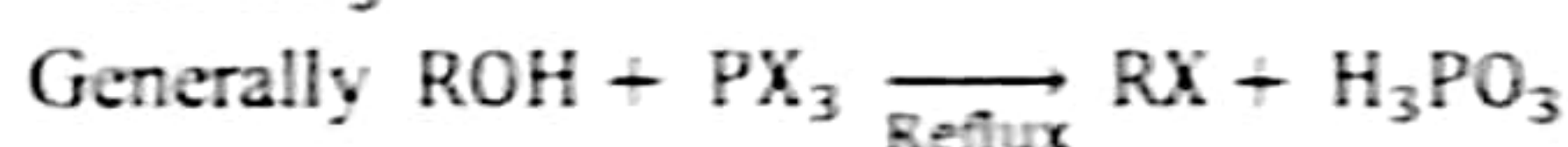
The main reaction under this heading is halogenation of alcohol.

(i) With PCl_5

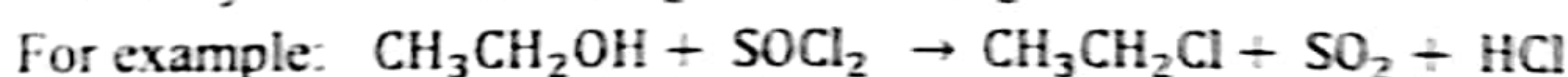
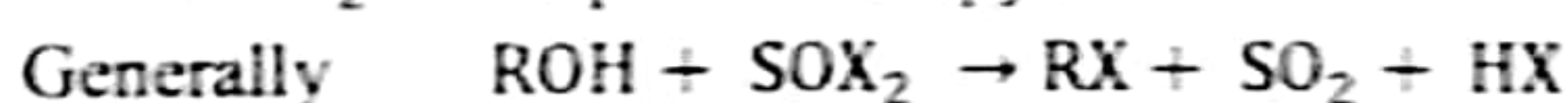


HCl evolved in the above reaction appears as misty fumes which produce dense white fumes with aqueous ammonia, so the reaction is used as a test of presence of OH group in the compound.

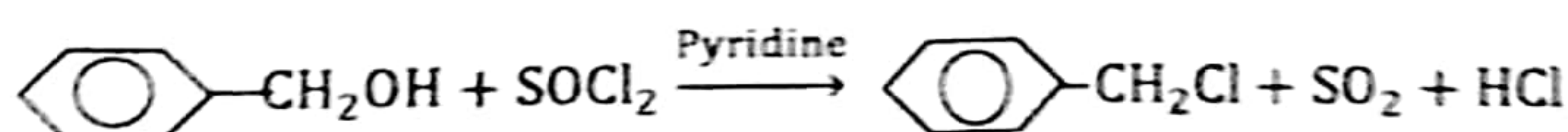
(ii) With PX_3



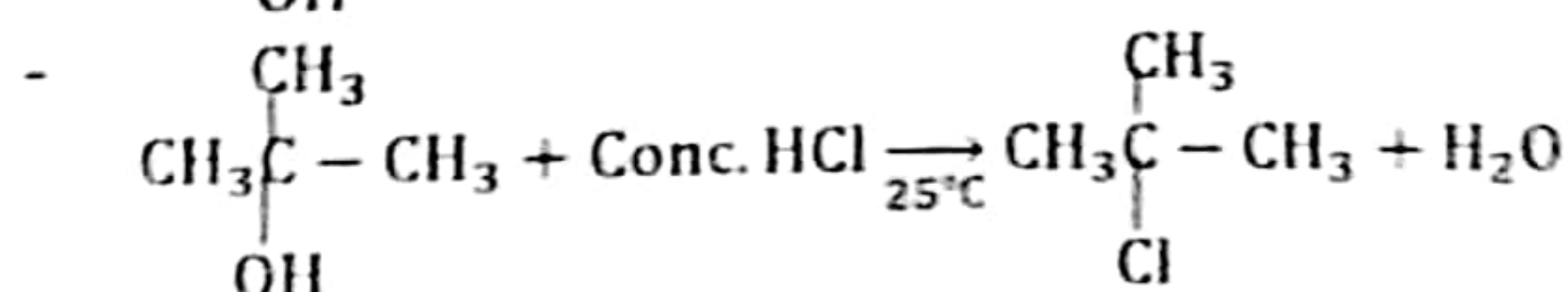
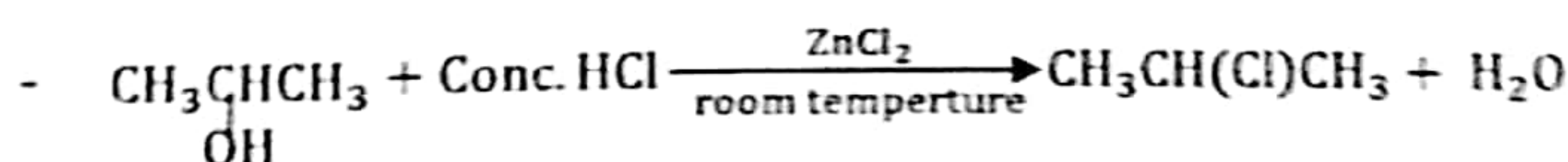
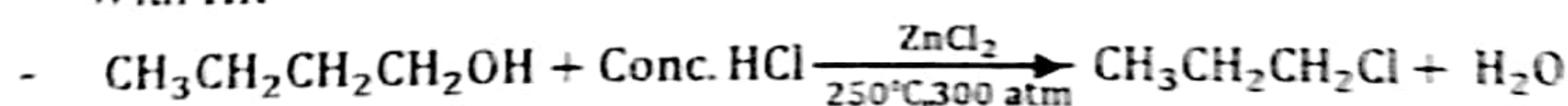
(iii) With SOX_2 under presence of pyridine.



Similarly,



(iv) With HX



The reactivity of alcohols in nucleophilic substitution reactions increase from 1°, 2° to 3° alcohols with 3° alcohols being most reactive; that is why 2° alcohol need only 25°C (room temperature) to

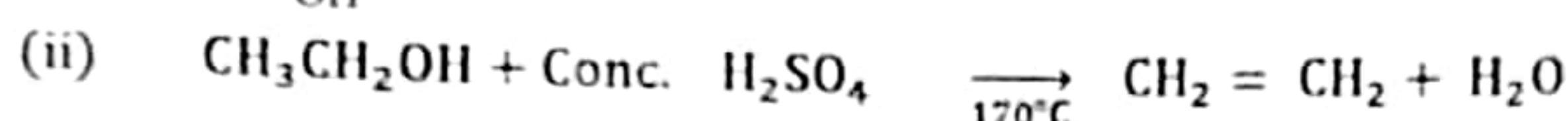
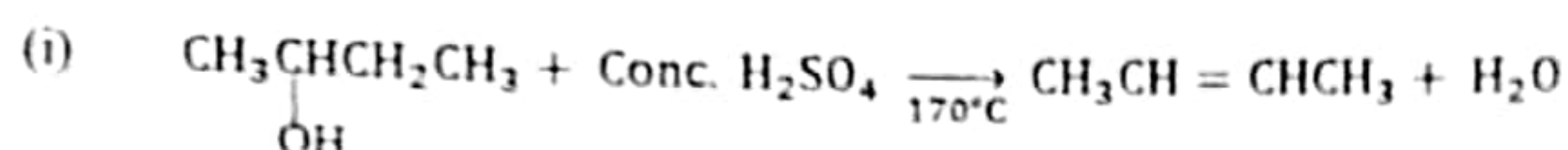
react with conc. HCl compared to 250°C which is required for 1° alcohol while in 3° alcohol even ZnCl₂ catalyst is not necessary.

- Also it should be noted that the reactivity of HX increases from HCl, HBr to HI with HI being most reactive, so when hydroiodic acid is applied instead of hydrochloric acid (or hydrobromic acid), there is no need of ZnCl₂ catalyst regardless to whether the alcohol is 1°, 2° or 3° alcohol.

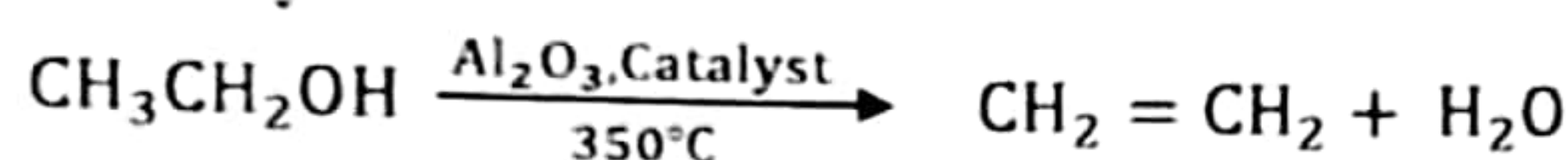
Reaction which involve OH group and β - hydrogen

Under this heading alcohol undergoes elimination reaction to form alkene.

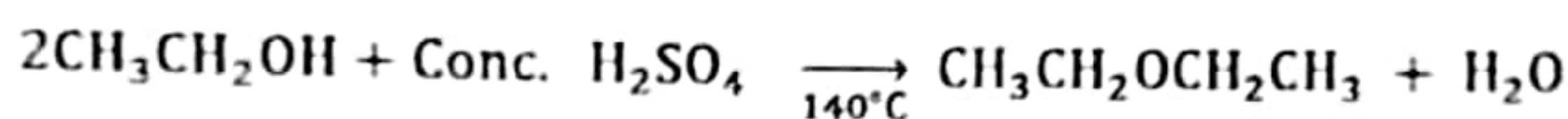
Example



Similarly

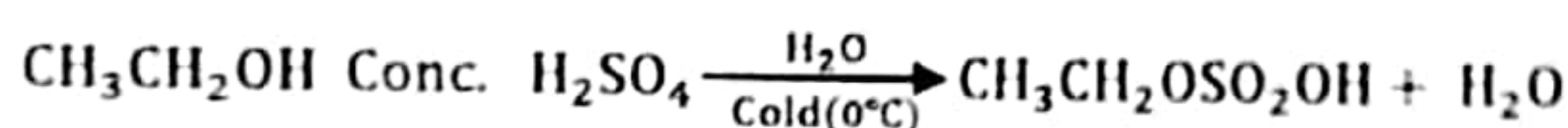


But

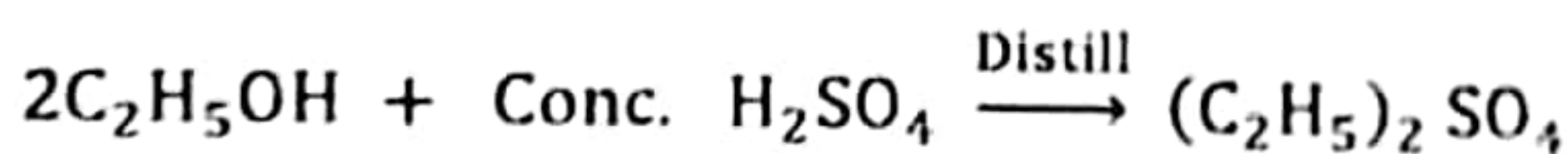


(The production of ether in above reaction is more favoured when H₂SO₄ is dilute).

But



But



In place of sulphuric acid, phosphoric acid which is also strong acid may be used to give alkene from alcohol.

The reader should understand that:

- The temperature required to cause elimination reaction decreases from primary alcohol to tertiary alcohol.

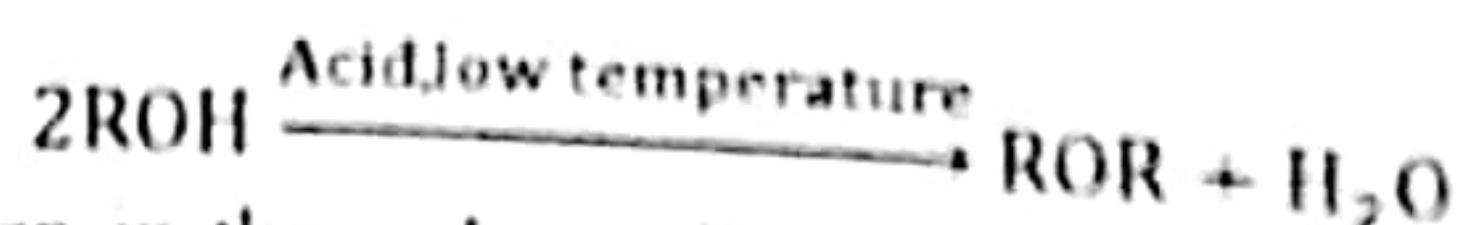
Primary (1°) alcohol requires 170°C – 180°C

Secondary (2°) alcohol requires 100°C – 140°C

Tertiary (3°) alcohol requires 25°C – 80°C

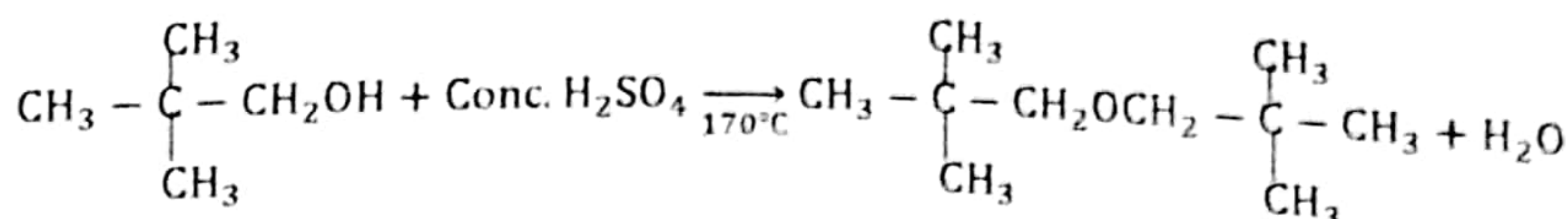
To ensure high yield of alkene, the acid must be in excess and the temperature must be sufficient.

- If the temperature is insufficient (or the alcohol is in excess), partial dehydration occurs and ether is formed.



Also if there is no α - hydrogen (hydrogen in the carbon adjacent to carbon with OH) there is no possibility of forming alkenes (elimination product); ether is formed in most cases.

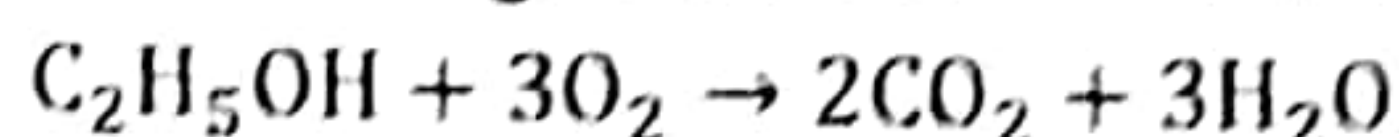
For example:



Oxidation

a) Combustion

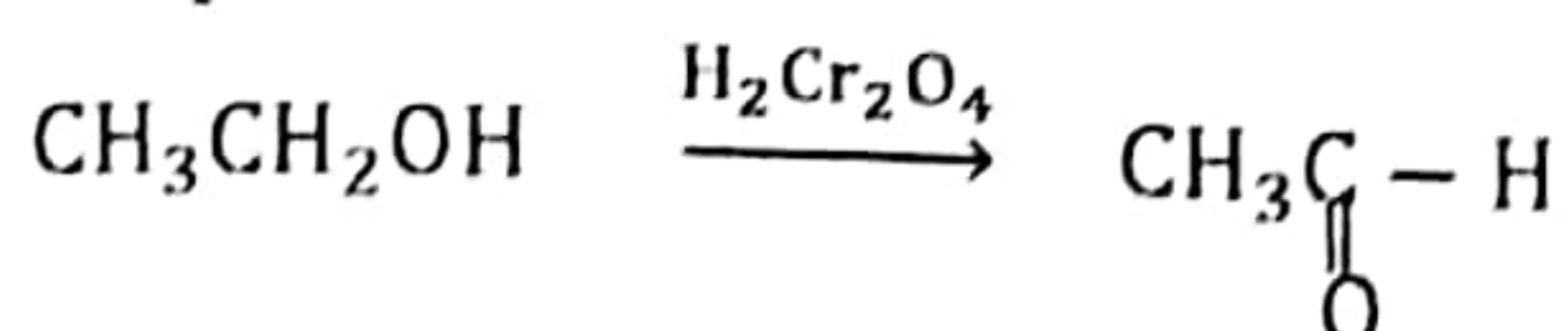
Ethanol burns in air with a pale blue flame to give carbon dioxide and water.



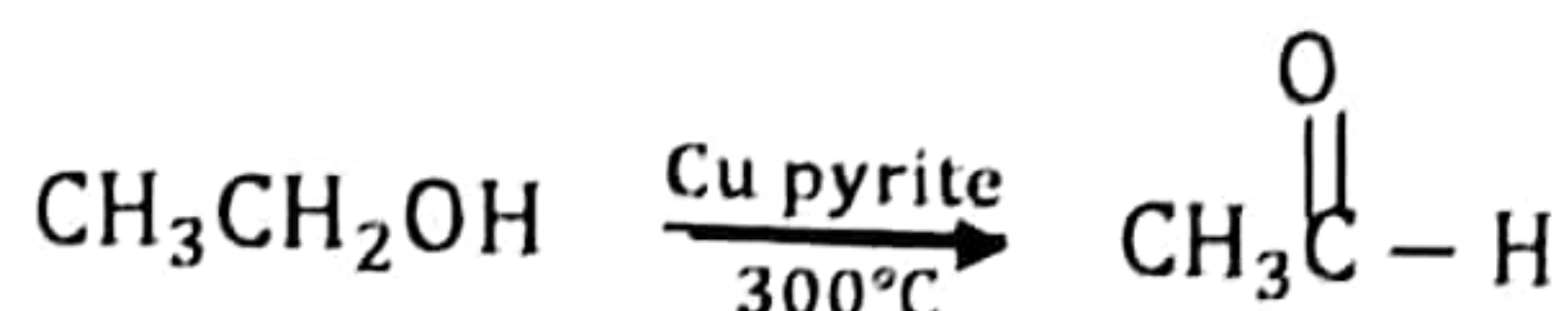
b) By oxidising agents

With weak oxidizing agent like $\text{H}_2\text{Cr}_2\text{O}_4$ primary alcohol tend to form aldehyde

Example

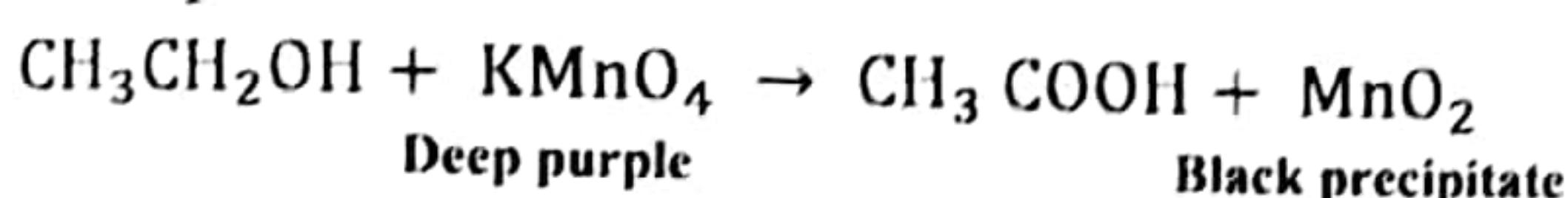


Also



With strong oxidizing agent like KMnO_4 , carboxylic acid is formed

Example

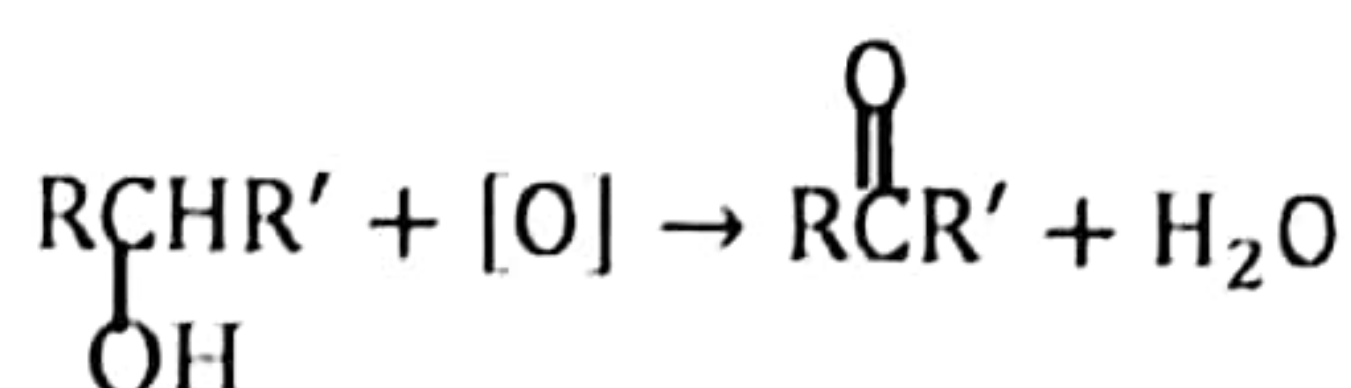


Deep purple

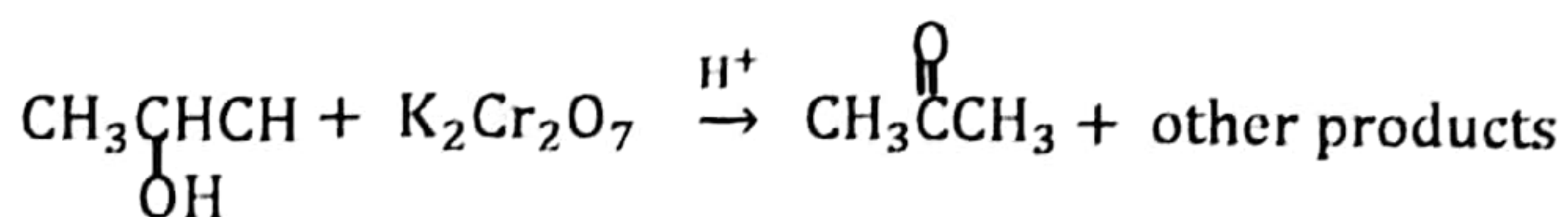
Black precipitate

With either weak or strong oxidizing agent secondary (2°) alcohol form ketone (unlike aldehydes, ketones resist further oxidation)

Generally;

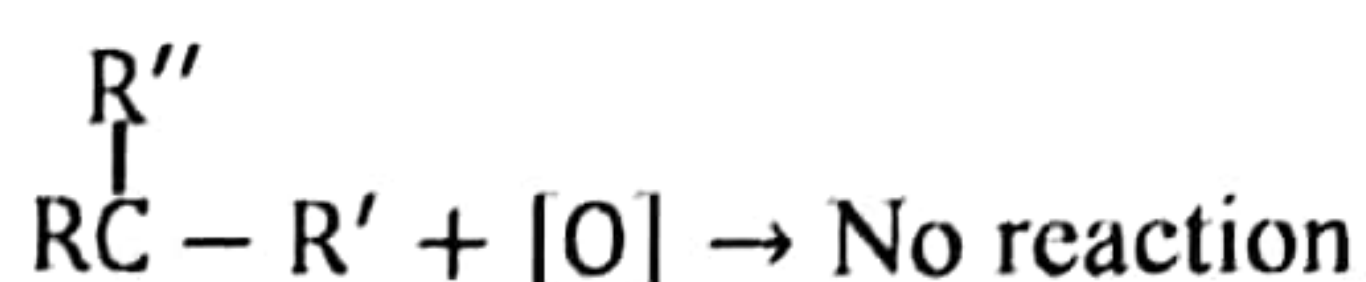


Example



Note:

Tertiary alcohols resist oxidation since there is no removable hydrogen in the carbon with OH.

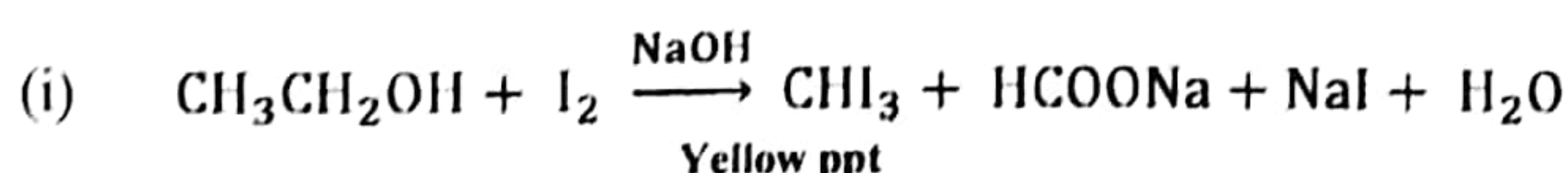


c) Iodoform test

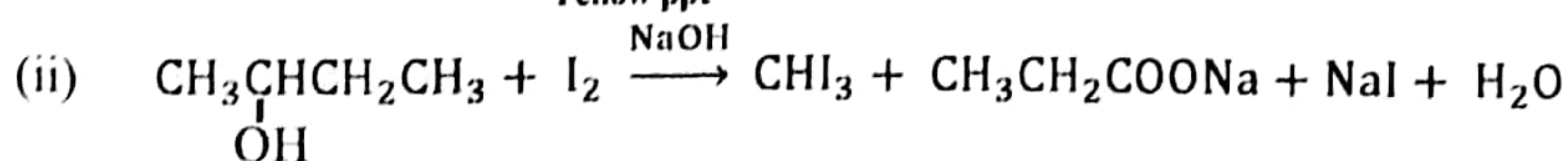
This is the chemical test for presence of terminal methyl group which is directly bonded the carbon with OH group (or to carbonyl group in the case of carbonyl compounds) by giving yellow precipitate of trichloromethane (iodoform), CHI_3 . (Actually it is another oxidation reaction)

- When compounds with terminal methyl group bonded to carbon with OH group is heated with I_2 in presence of NaOH they give yellow precipitate of iodoform.

Example

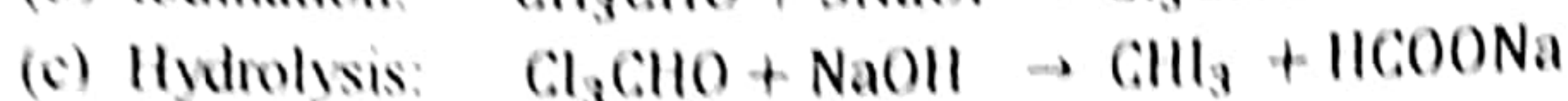
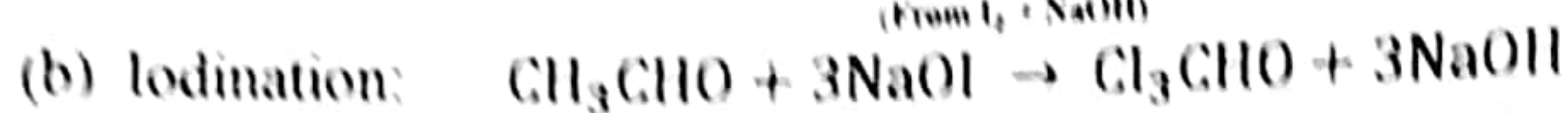
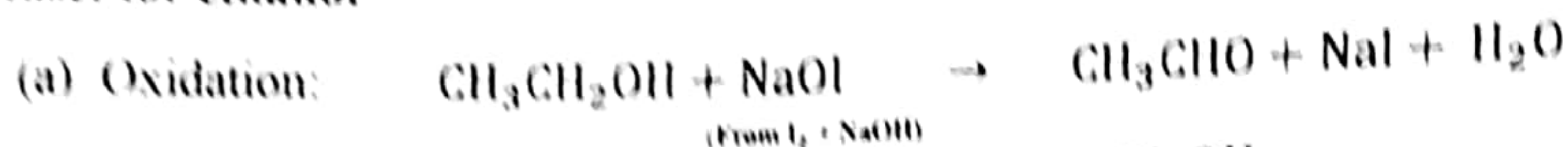


Yellow ppt

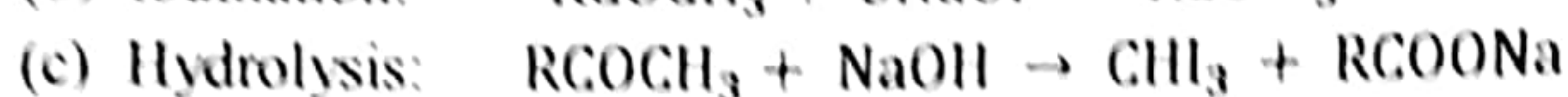
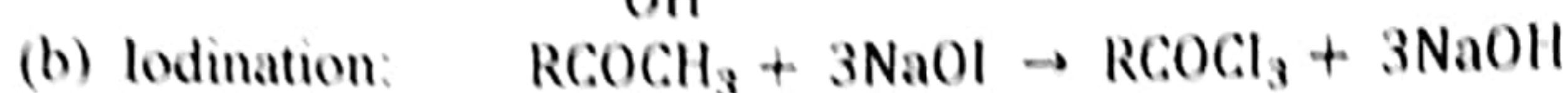
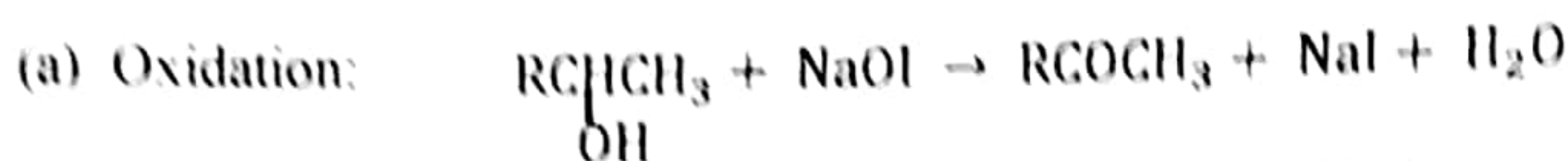


Actually reaction follows the following steps:

1st case: for ethanol



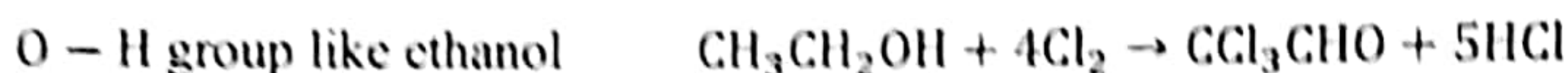
2nd case: For secondary methyl alcohol



For primary alcohol, only ethanol give positive iodoform test while for secondary alcohols, all methyl alcohols ($\text{R} - \text{CH}(\text{OH}) - \text{CH}_3$) gives positive iodoform test.

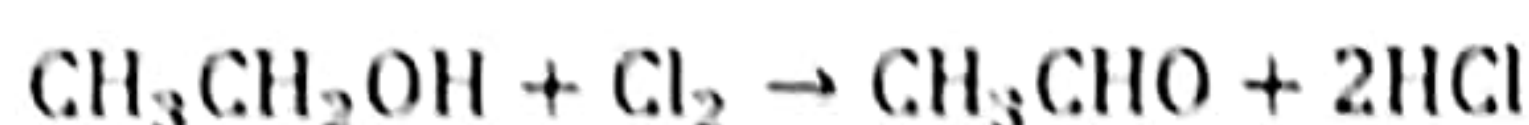
It should be understood that:

Chlorine even in absence of NaOH can react with alcohol with methyl group bonded with



The reaction occurs in two steps as shown below

First step: Oxidation



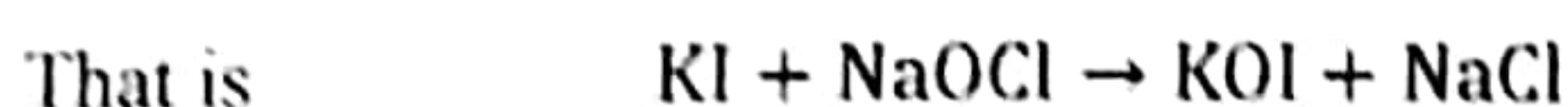
Second step: Chlorination



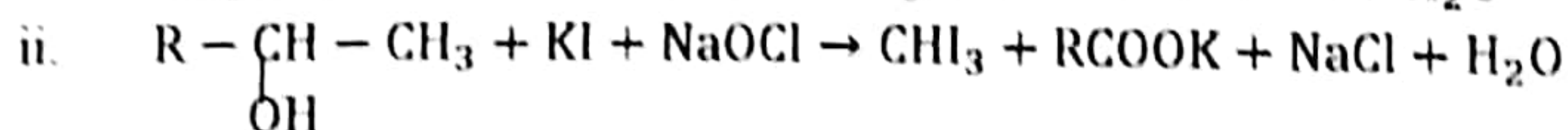
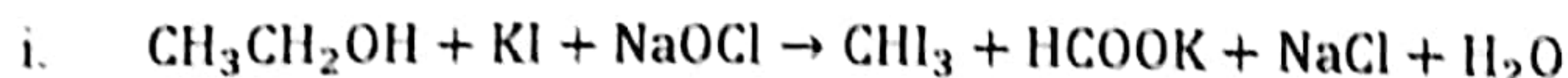
Bromine and iodine being weaker oxidizing agent, has no action unless an alkali like NaOH is present.

Futhermore:

Iodoform reaction can also be carried out by using mixture of potassium iodide (KI) and sodium hypochlorite (NaOCl) because the mixture produce KOI which reacts like NaOI in the above mechanism.



And hence:

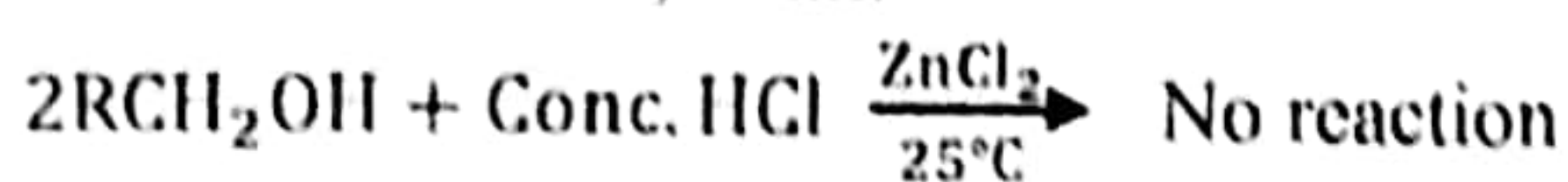


Chemical test to distinguish between primary, secondary and tertiary alcohols

Three classes of alcohols can be distinguished by using Lucas reagent.

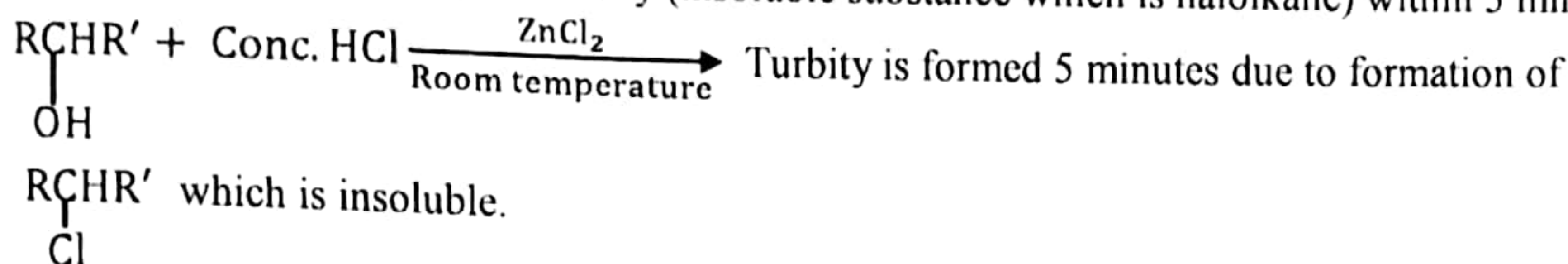
Lucas reagent is the mixture of concentrated HCl and ZnCl_2 solution, mixed at equal proportion.

– With Lucas reagent at room temperature, primary alcohol does not form cloudiness or turbidity (insoluble substance) at all.

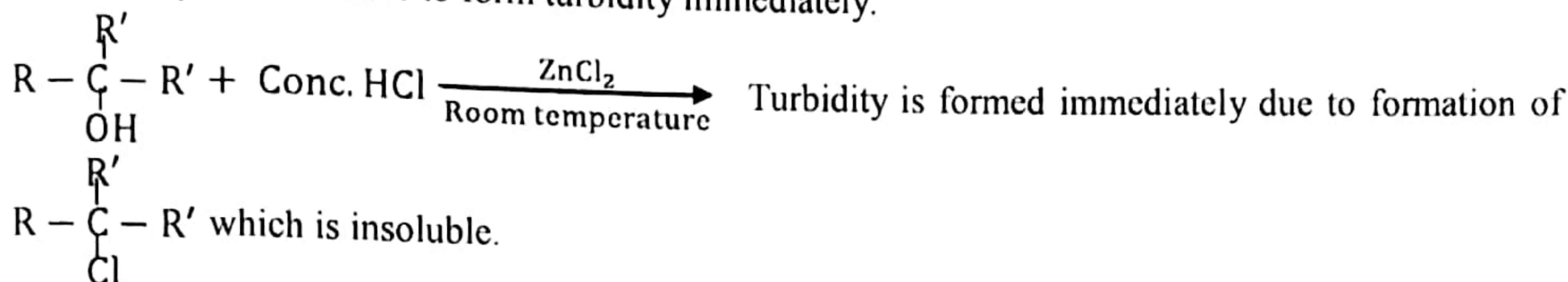


(No formation of turbidity which is insoluble substance)

- Secondary alcohol tends form turbidity (insoluble substance which is haloalkane) within 5 minutes.



- Tertiary alcohol tends to form turbidity immediately.



Example 4

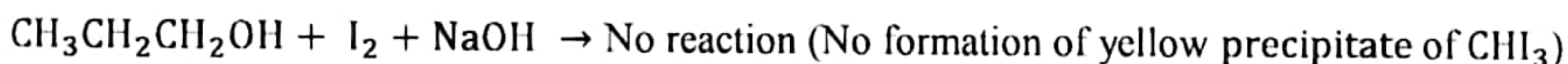
Give chemical test to distinguish between:

- Ethanol and propanol (1 test)
- Butan-1-ol and butan-2-ol (2 test)
- Butan-2-ol and 2-methylpropan-2-ol (2 test apart from using Lucas reagent)

Solution

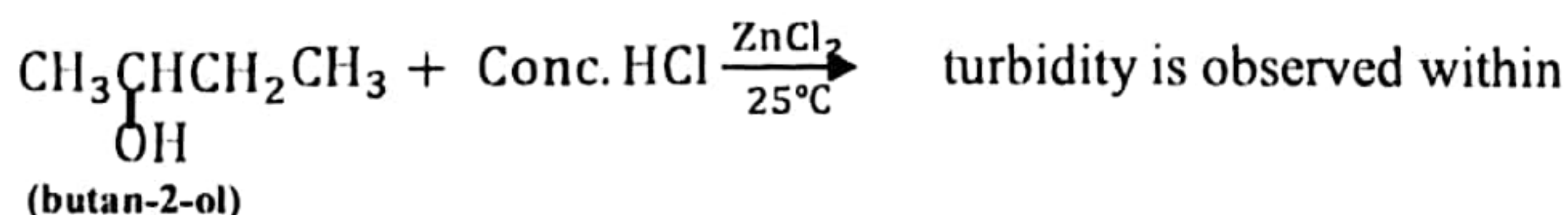
(i) Ethanol give positive Iodoform test while propanol give negative iodoform test.
i.e. $\text{CH}_3\text{CH}_2\text{OH} + \text{I}_2 + \text{NaOH} \rightarrow \text{Yellow precipitate of CHI}_3(\text{iodoform})$
(ethanol)

While



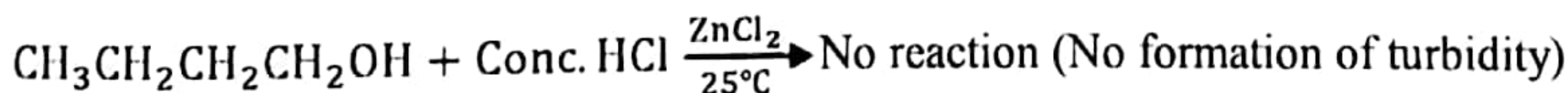
(ii) 1st test

With Lucas reagent at room temperature butan-2-ol give turbidity (cloudiness) within 5 minutes while butan-1-ol does not give turbidity at all



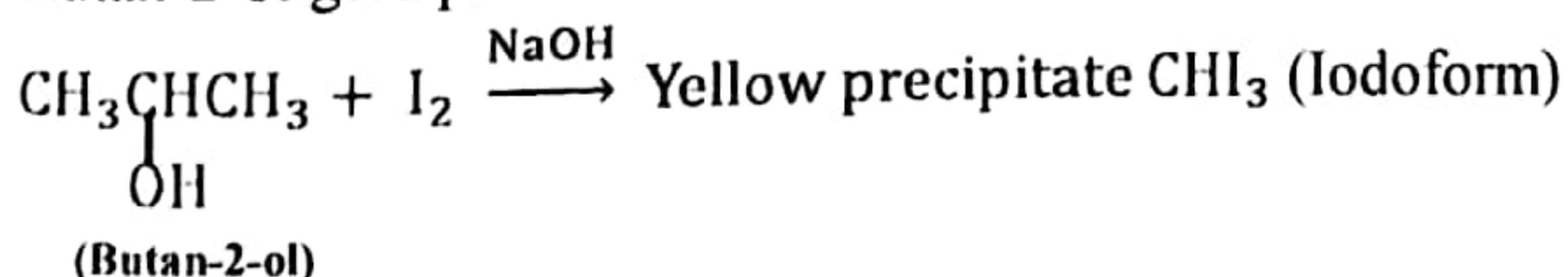
5 minutes due to the formation of $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$ which is insoluble

While

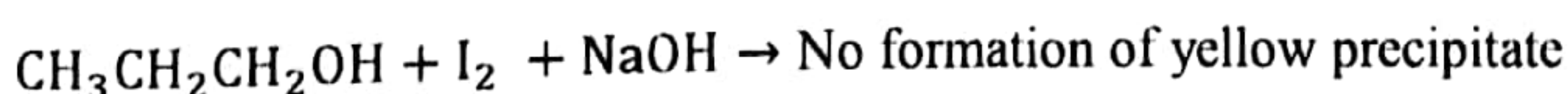


2nd test (Iodoform test)

Butan-2-ol give positive iodoform test while butan-1-ol give negative iodoform test



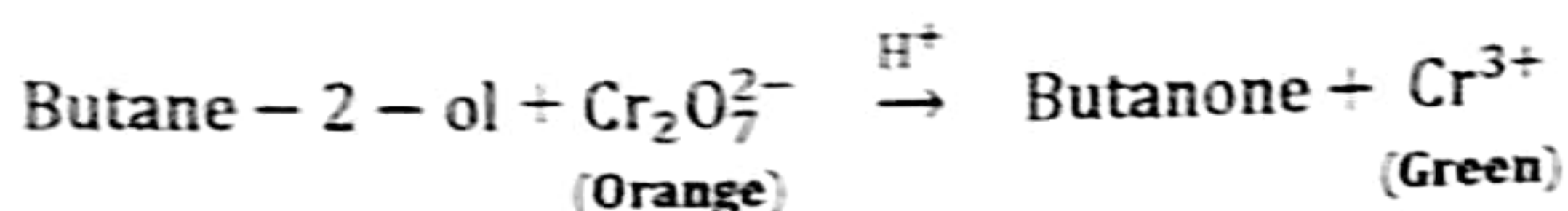
While



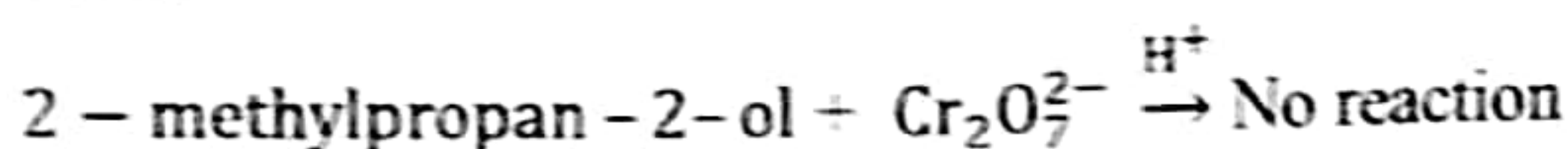
(iii) 1st test

When butan-2-ol (2° alcohol) is mixed with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, the orange colour of $\text{K}_2\text{Cr}_2\text{O}_7$ is changed to green while 2-methylpropan-2-ol (3° alcohol) does not show any colour change.

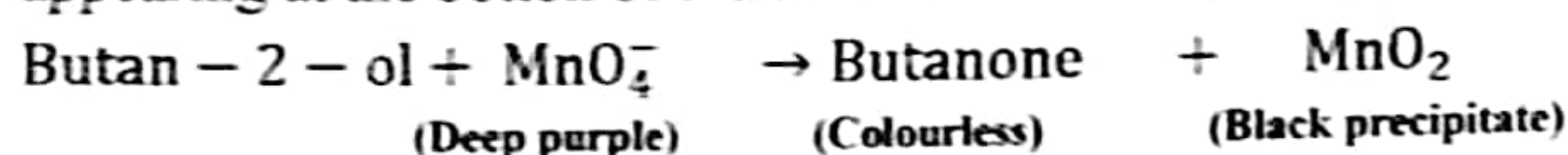
i.e.



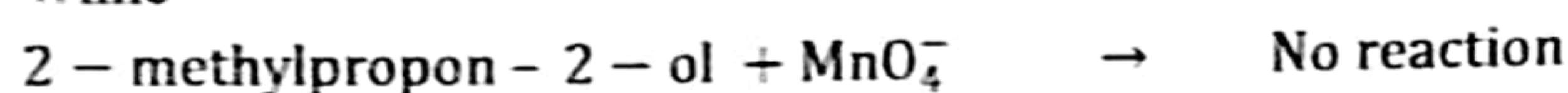
While

**2nd test**

Butane-2-ol decolourises KMnO_4 which is deep purple to form black (or brown) precipitate appearing at the bottom of the beaker while 2-methylpropan-2-ol does not.



While

**Example 5**

An organic compound 'P' $\text{C}_4\text{H}_{10}\text{O}$ reacts with PCl_5 to form an organic compound 'Q', inorganic compound 'N' and gas 'R' which produce dense white fumes with aqueous ammonia. 'P' also reacts with a mixture of iodine and NaOH forming sodium salt 'W' and triiodomethane.

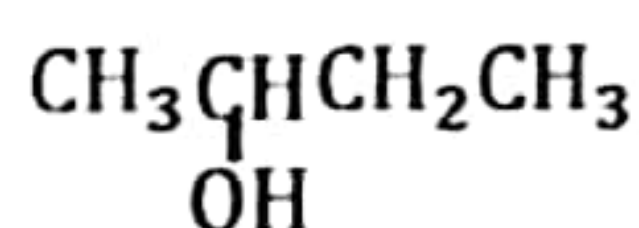
- Identify and write the structure formula of compound P, Q, R and W.
- Write an equation of each of the above reaction

Solution

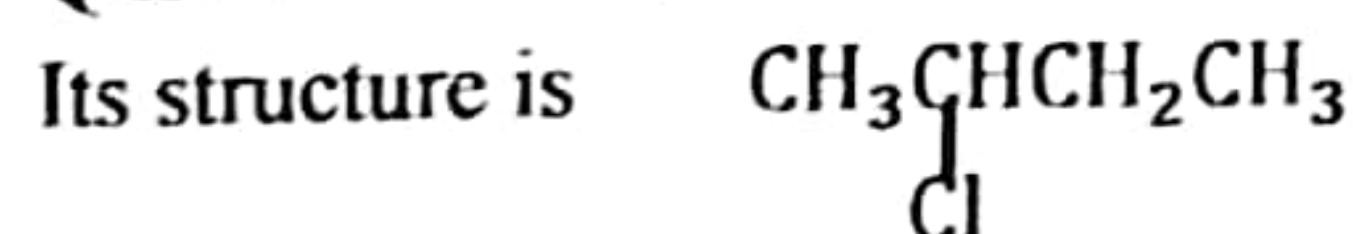
- The molecular formula of P $\text{C}_4\text{H}_{10}\text{O}$ confirms general molecular formula of P is $\text{C}_n\text{H}_{2n+2}\text{O}$. Thus P is either alcohol or ether.

- A gas which produce dense white fumes with aqueous ammonia is HCl
- So since the reaction of 'P' and PCl_5 produce HCl there is OH group in P. Thus P can not be an ether, it must be an alcohol.
- Since compound "P" reacts with mixture of iodine and NaOH to give triiodomethane then compound "P" give positive iodoform test.
- Hence in "P" there is terminal methyl group bonded to carbon with OH group.

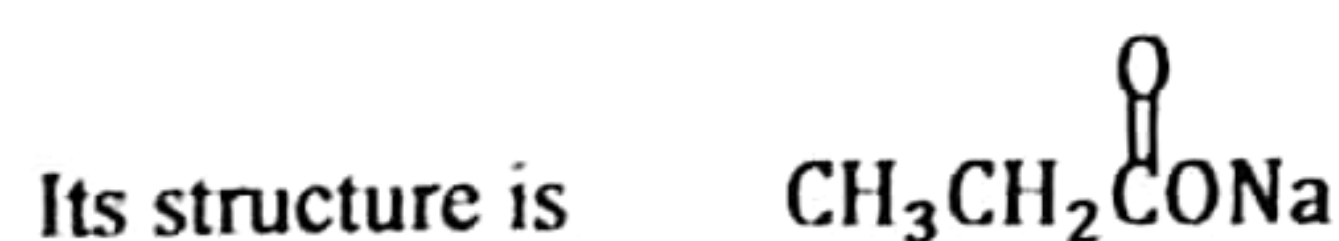
Thus its structure is



Q is 2-chlorobutane

N is POCl_3 R is HCl

W is sodium propanoate



- Refer to the text.

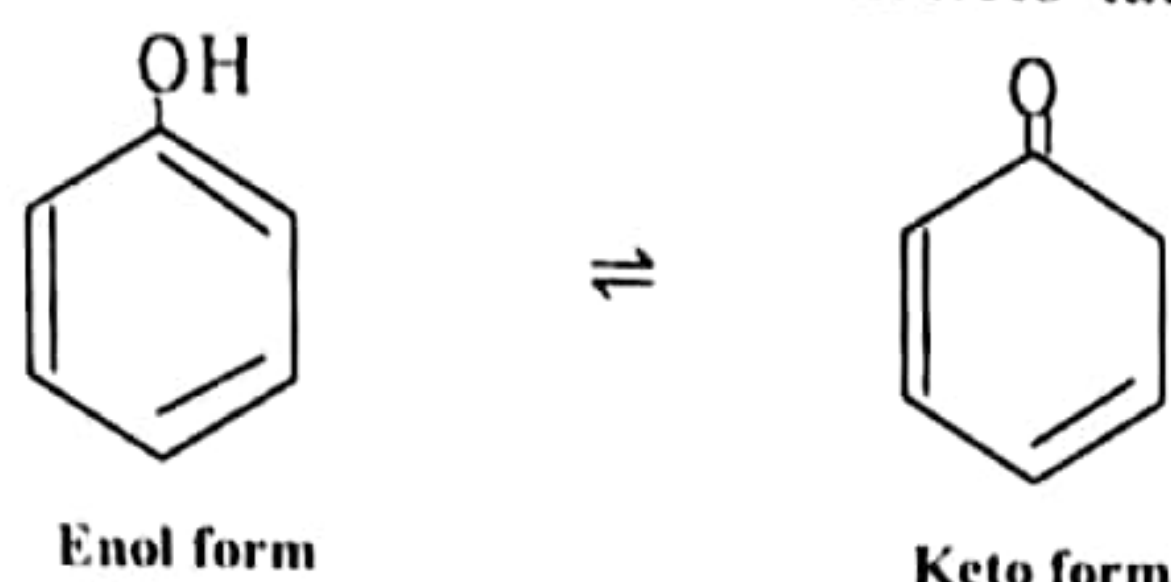
CHEMICAL REACTIONS OF PHENOL

Generally chemical reactions of phenol can be divided into two types;

- Electrophilic substitution reactions on a side OH group
- Electrophilic substitution reactions in benzene ring

It should be noted that:

- Like halobenzene, phenol is reluctant to nucleophilic substitution reaction whereby the whole OH group should be removed for the same reason of mesomerism which leads to the formation of C = O between carbon in the benzene ring and O of OH in phenolic group. To break this bond is more difficulty than breaking C – O bond in alcohol.
- Phenol can tautomerise to form keto-tautomer as per equation;

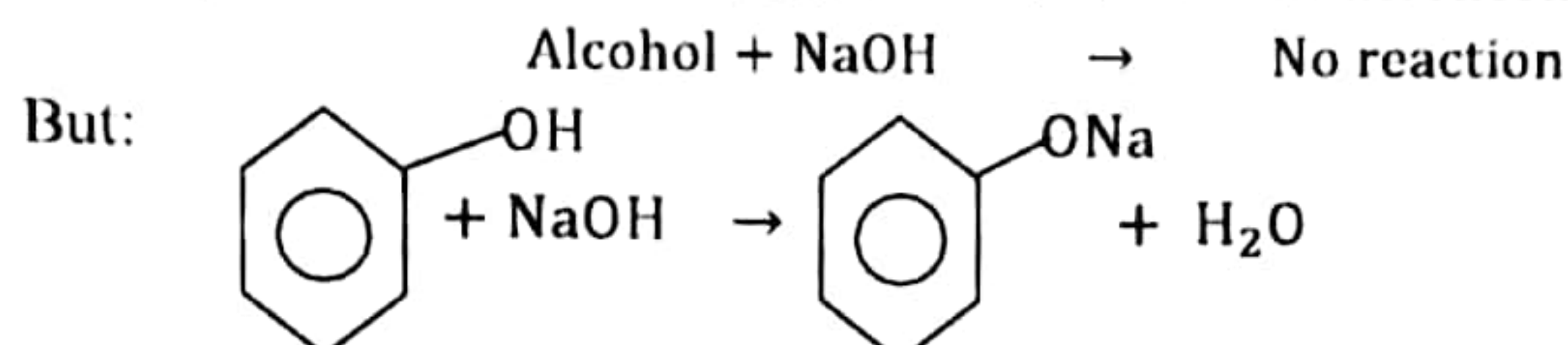


However the keto form is highly unstable due to destabilisation resulting from loss of aromaticity.

Electrophilic substitution reaction on a side OH group

a) Reaction with alkaline solution

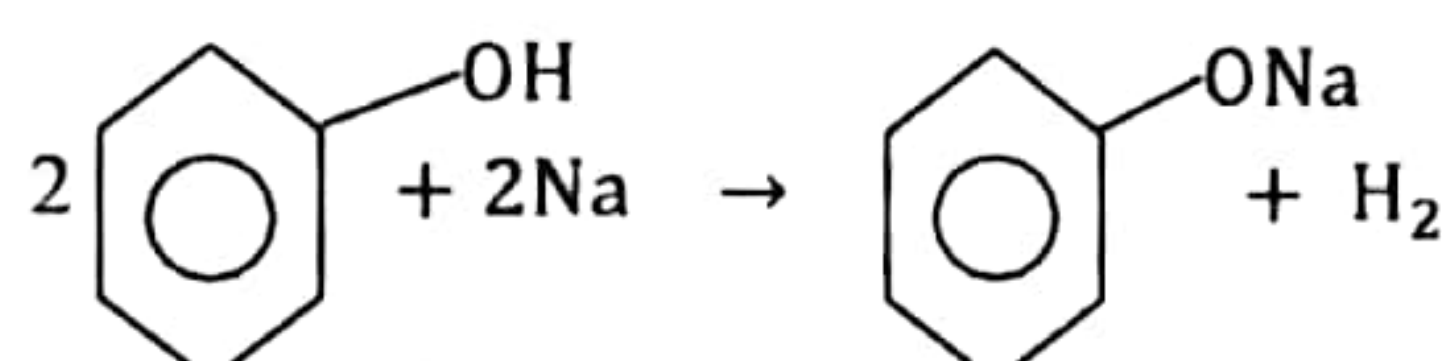
Unlike alcohol, phenol reacts with alkaline solution like NaOH i.e. Alcohol + Alkaline solution, e.g.



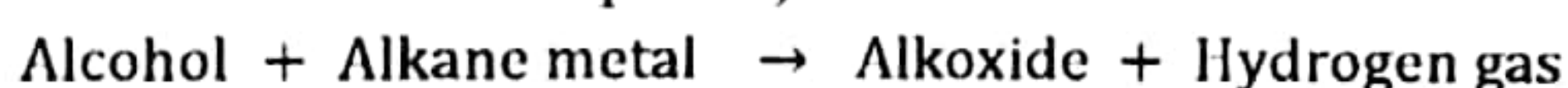
The reaction gives one of the differences between alcohol and phenol.

b) Reaction with alkaline metals

Phenol reacts with alkaline metals like Na, K, Li etc to form phenoxide and hydrogen gas is evolved
Example;

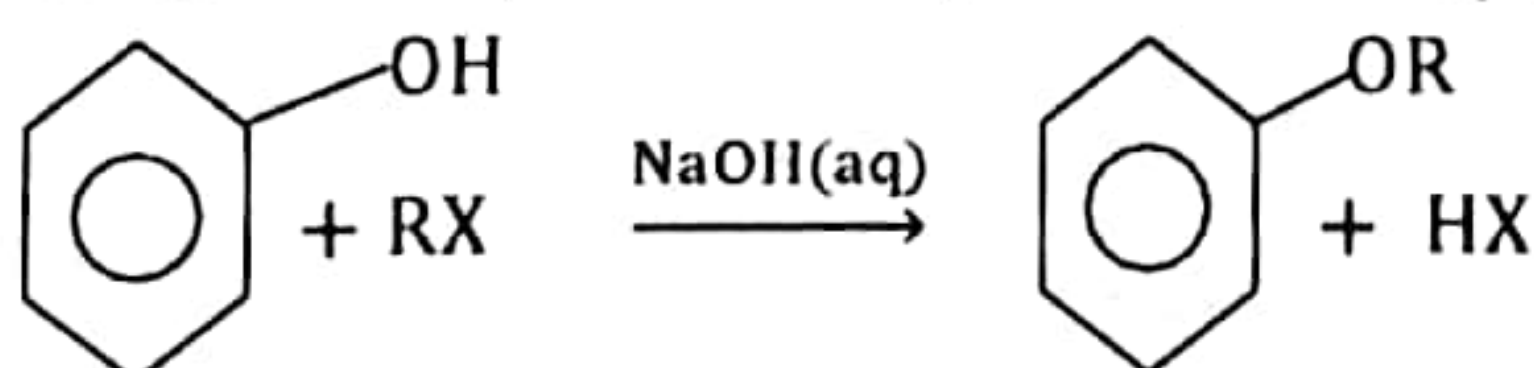


The reaction show one of the similarities between alcohol and phenol (and it give one of acidic characters of both alcohols and phenol).

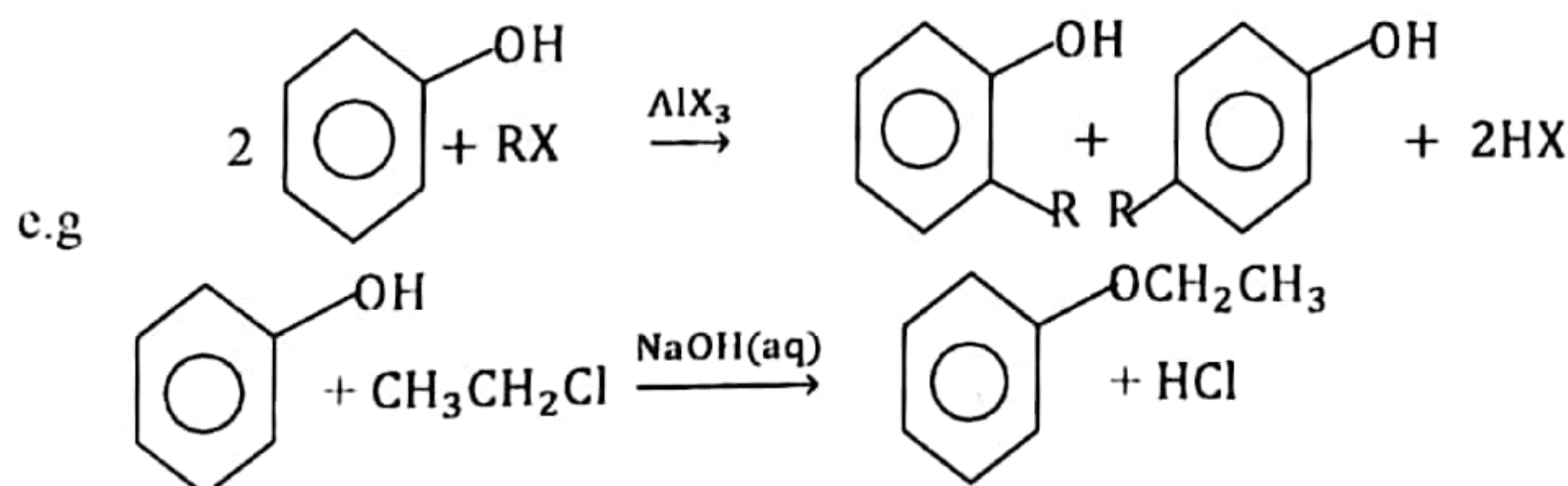


c) Formation of ether

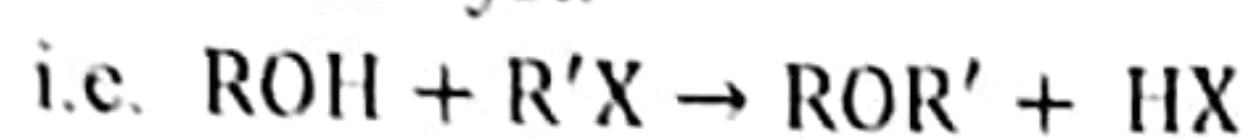
Phenol reacts with halolalkane in presence of aqueous sodium hydroxide catalyst to form ether.



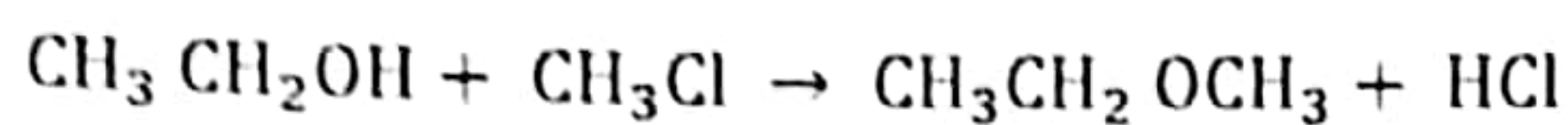
But



The reaction shows another similarity between alcohol and phenol although in alcohol there is no need NaOH catalyst.



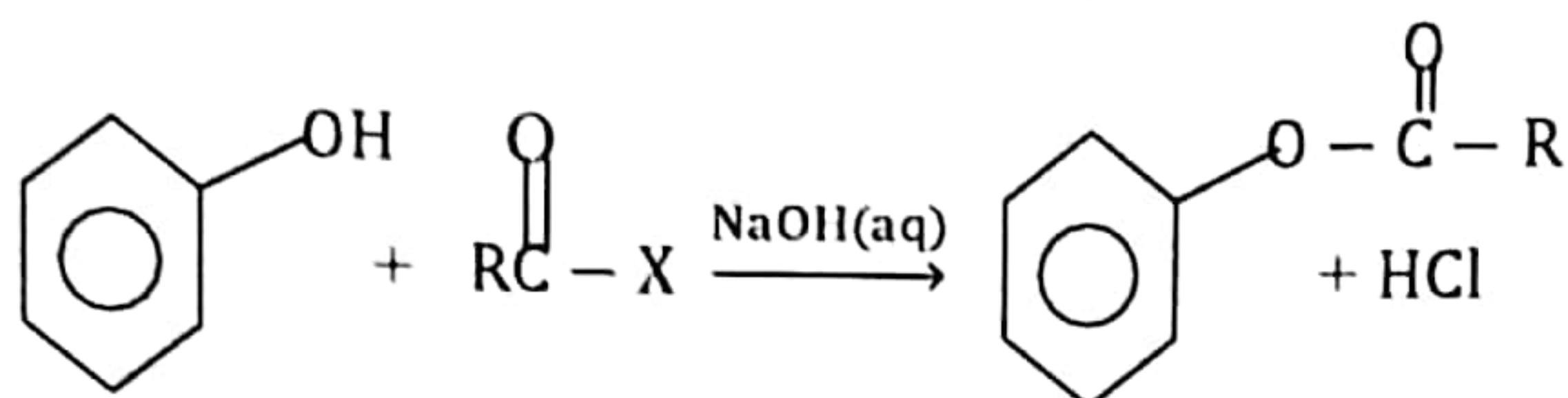
Example,



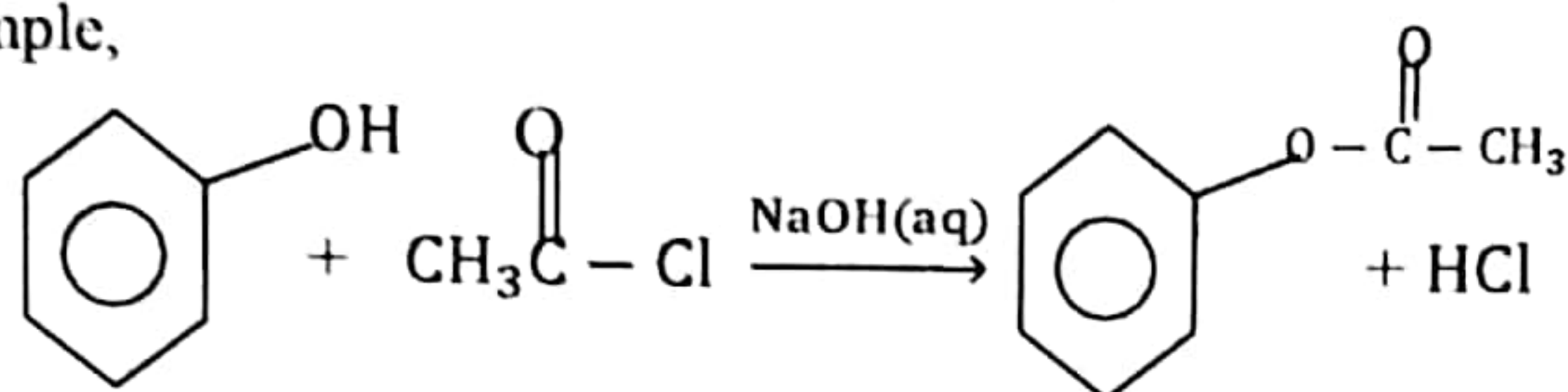
d) Formation of Ester

Phenol reacts with acyl compounds in presence of NaOH (aq) catalyst to form ester.

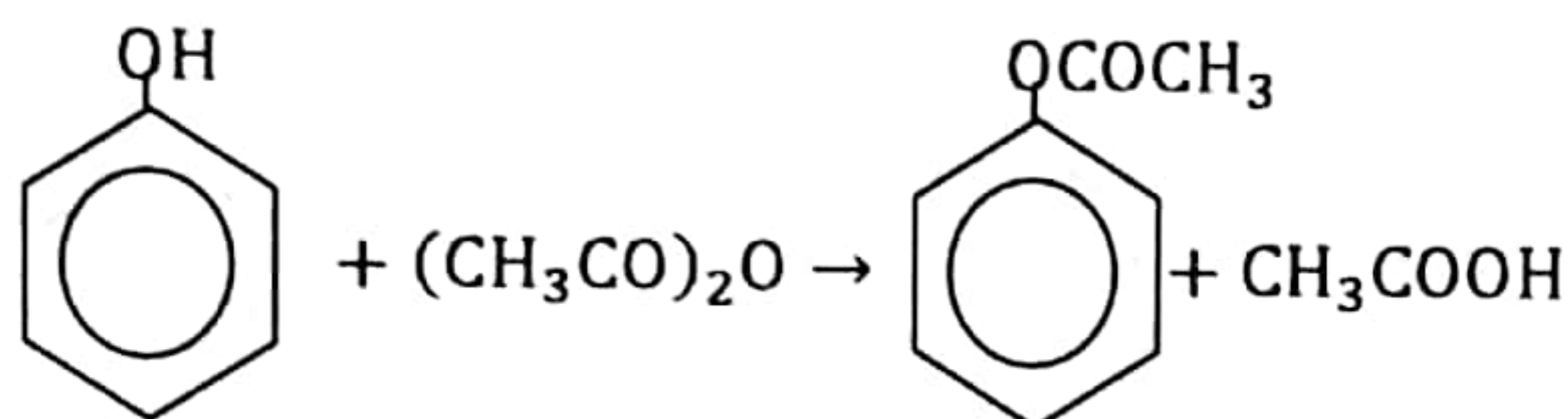
i.e.



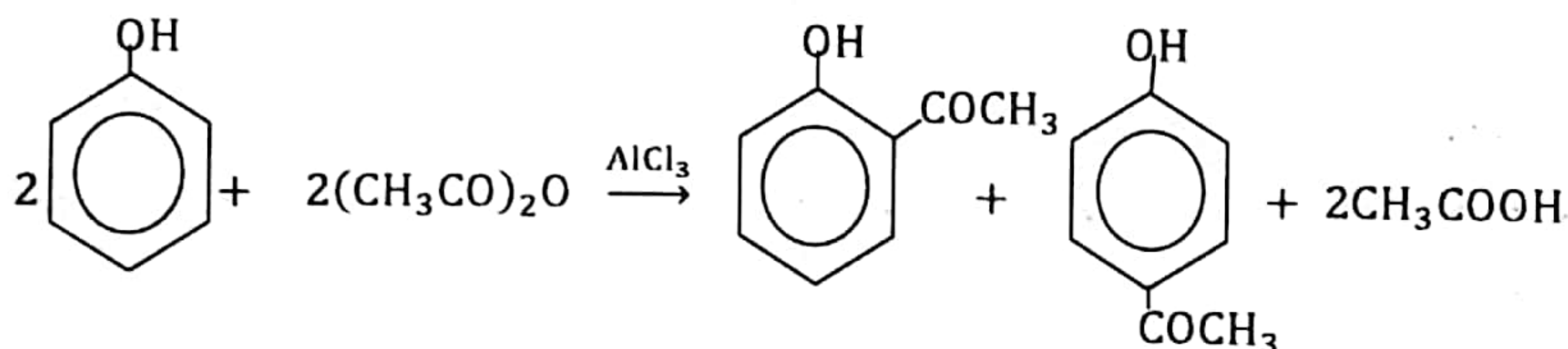
Example,



Similarly:

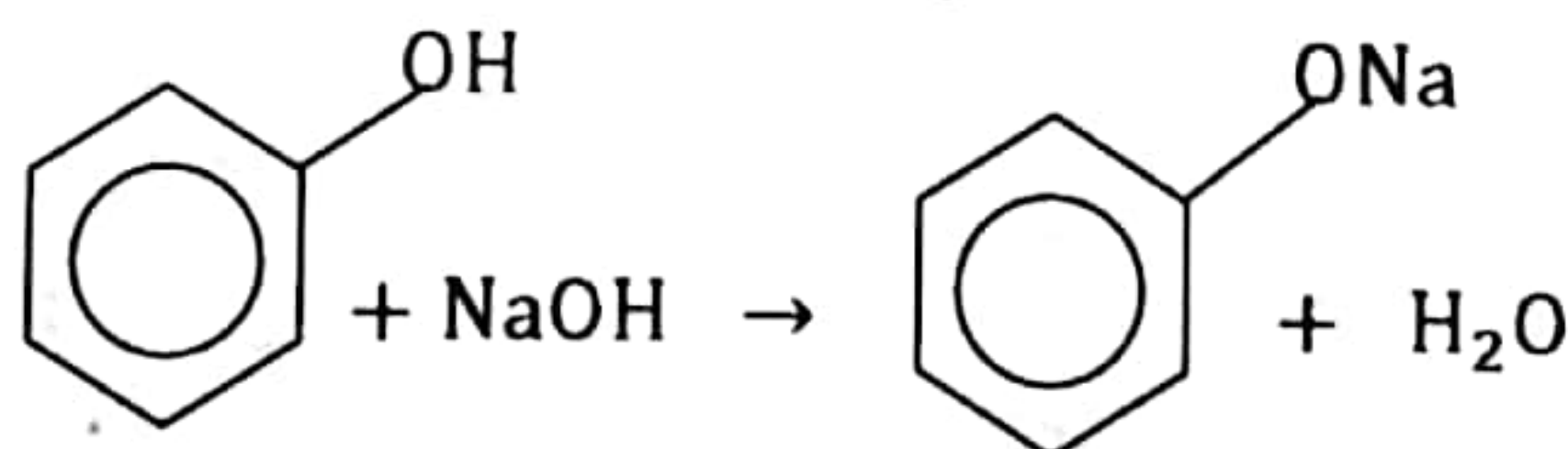


But

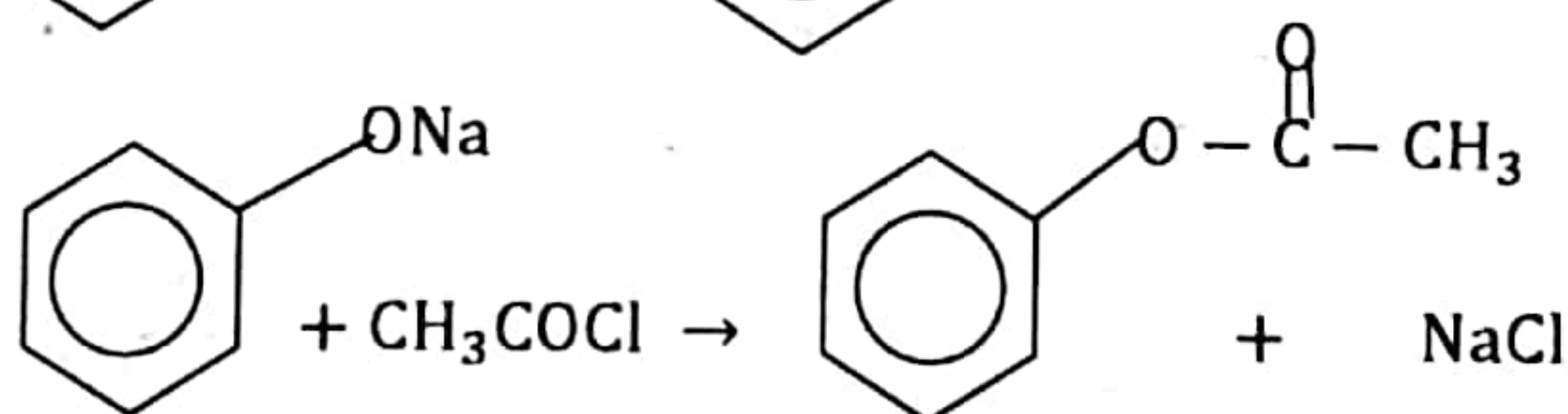


The use of NaOH (aq) in the above reaction is to convert phenol into sodium phenoxide which has quicker reaction with the acyl compound than phenol.

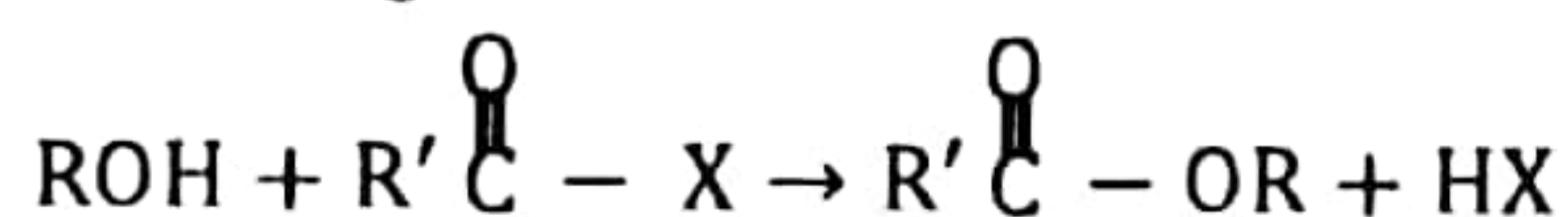
That is



Then

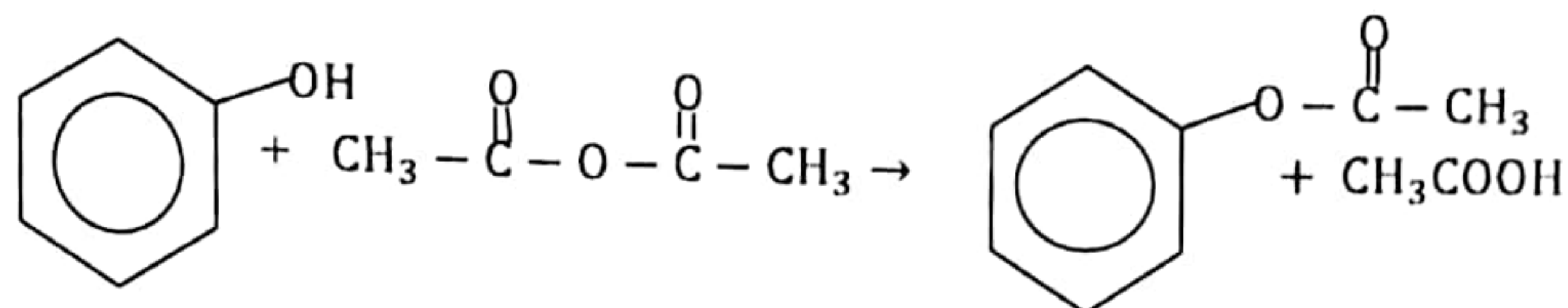


The reaction shows another similarity between alcohol and phenol. Alcohol also reacts with acyl compounds to form ester although in alcohol there is no need of NaOH

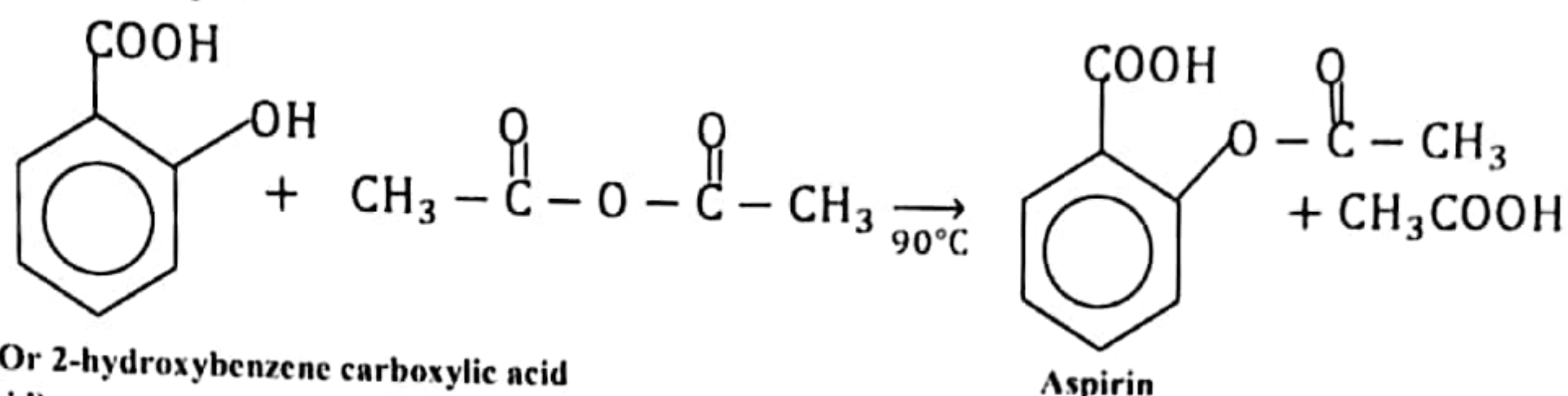


It should be noted that:

Phenol can also react with acid anhydride to give aromatic ester. e.g.



The reaction is very important in manufacturing of aspirin from 2-hydroxybenzoic acid (common name is salicylic acid) as per equation



2-hydroxybenzoic acid Or 2-hydroxybenzene carboxylic acid
(Common name: salicylic acid)

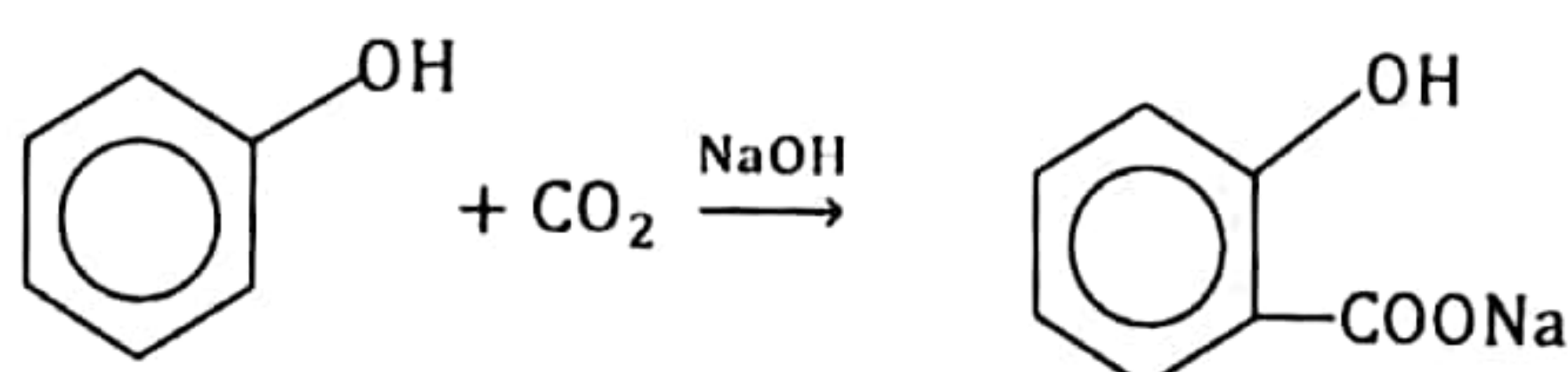
The above reaction can also be carried by using ethanoyl chloride (acyl compound with formula CH_3COCl).

However ethanoic anhydride (acid anhydride with formula $\text{CH}_3\text{COOCH}_3$) is more preferred to ethanoyl chloride, **why? Here are reasons!**

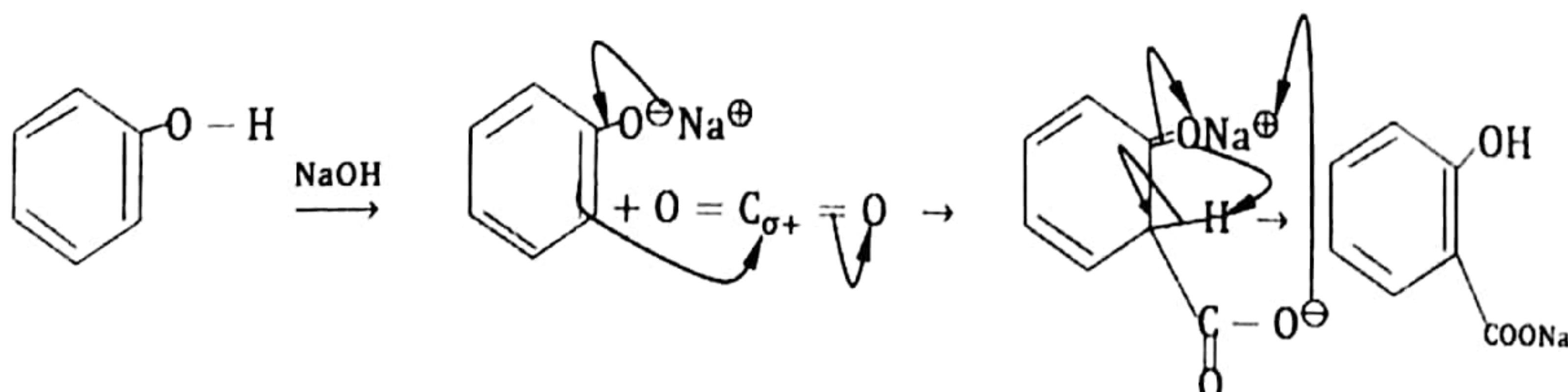
- Ethanoic anhydride is cheaper than ethanoyl chloride
- Ethanoic anhydride is safer to use than ethanoyl chloride as it is less corrosive and not easily hydrolyzed (its reaction with water is slower).
- Ethanoic anhydride does not produce dangerous fumes of hydrogen chloride which is corrosive and poisonous.

Kolbe-Schmidt reaction

This is the reaction between phenol and carbon dioxide in presence of solution of sodium hydroxide to give salt of salicylic acid



The reaction confirm the activating effect of OH group because CO_2 is so weak electrophile that cannot react with unsubstituted benzene. However under presence of OH substituent in the benzene which is activator, the reaction occurs per mechanism.



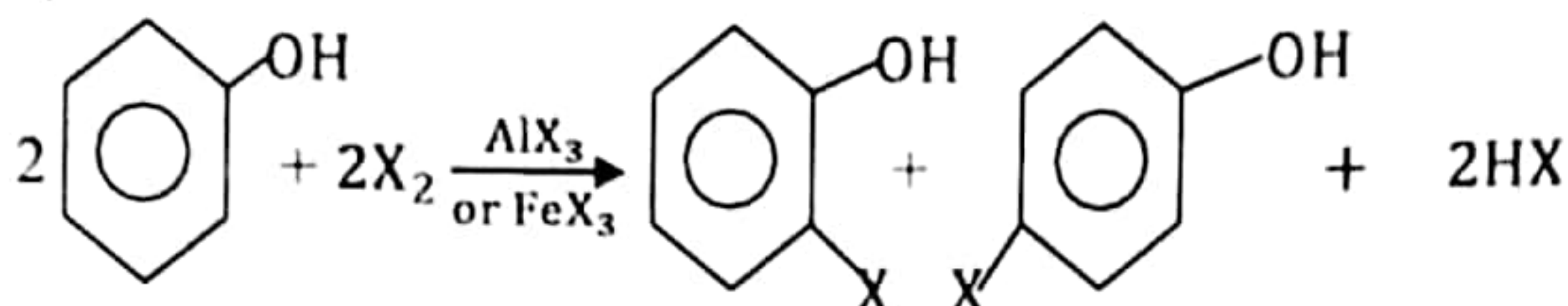
Electrophilic substitution reactions in benzene ring

Under this heading phenol reacts like benzene the only difference is that OH group in phenol directs an incoming electrophile at ortho para positions.

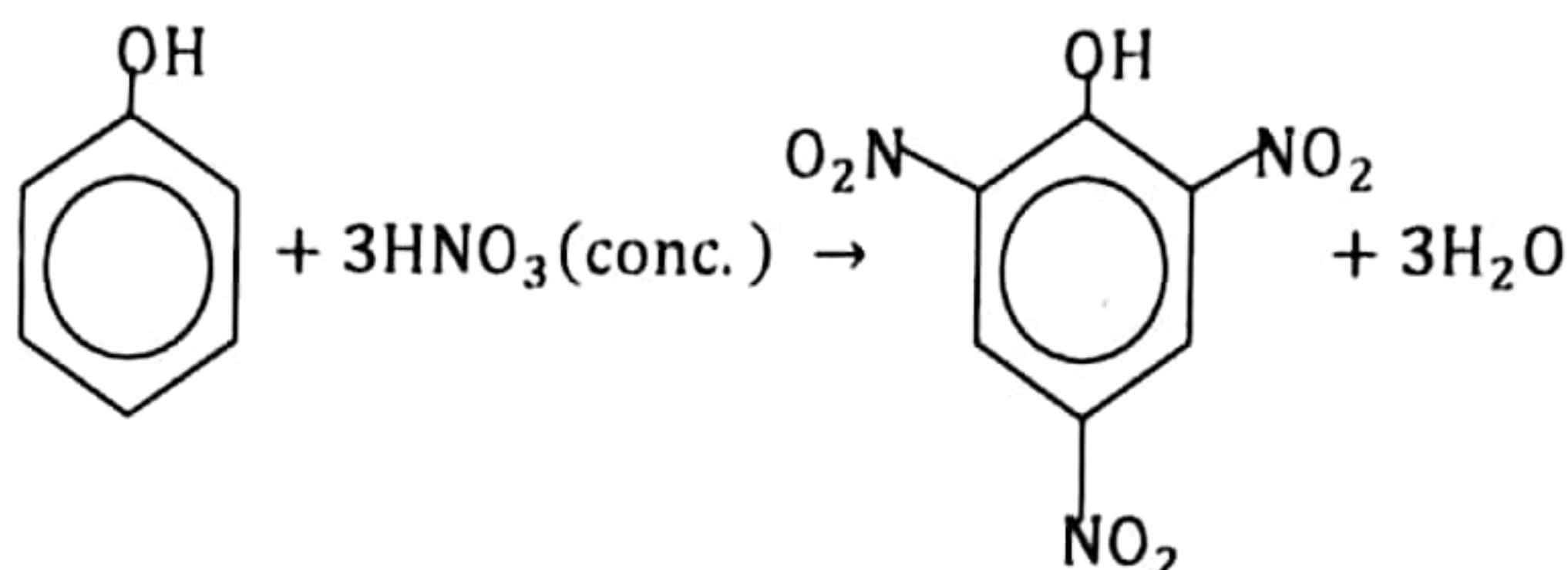
- In most cases the reaction can take place even in absence of Lewis acid because OH is strong activator.

Examples;

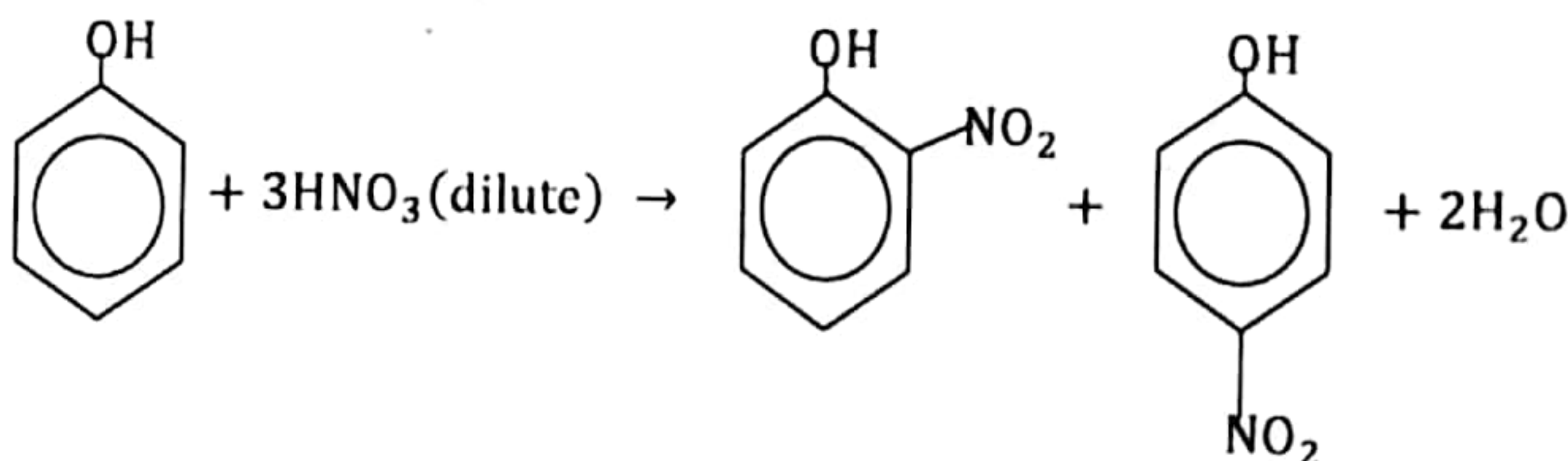
Alkylation



Reaction of phenol with concentrated HNO_3



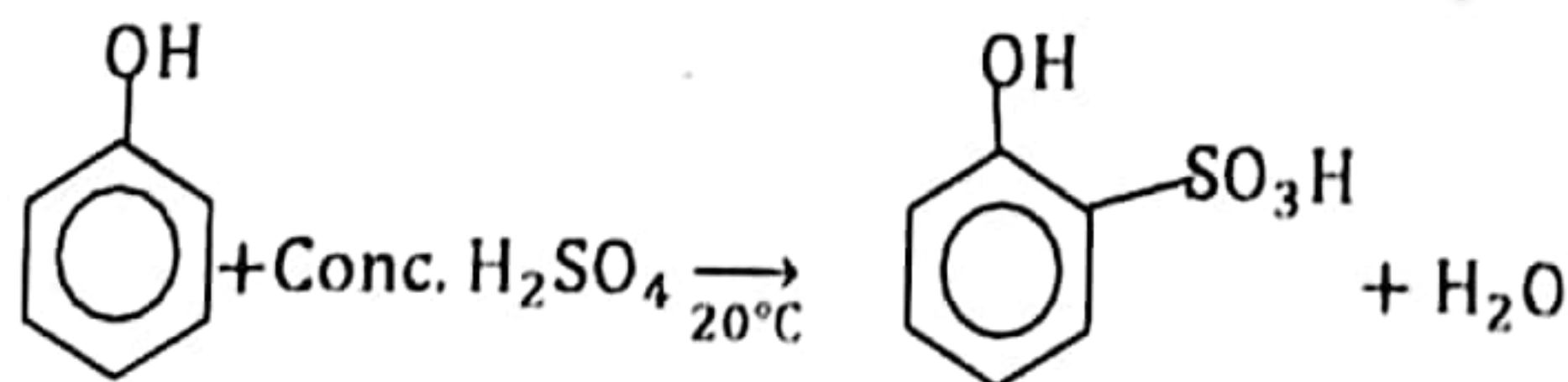
(Note: There is no need of Lewis acid catalyst because the OH group in phenol is good activator)
But



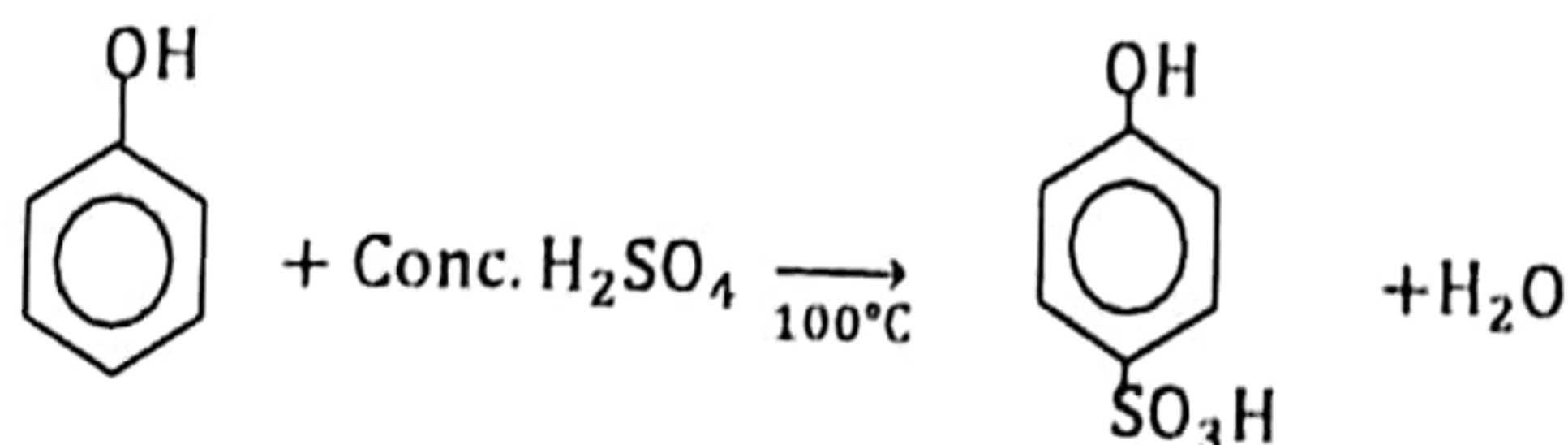
(Here **dilute** HNO_3 means there is only small amount of NO_2 (electrophile) produced and therefore the electrophilic substitution reaction occurs to smaller extent)

The reader should know that:

At low temperature, close to the room temperature, in most cases phenol gives ortho-product as major product while para product becomes the major product at high temperature. For example;

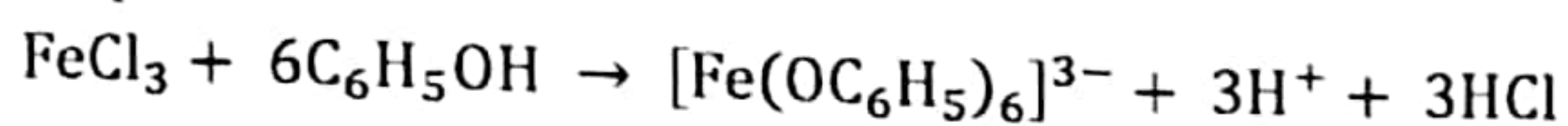


But



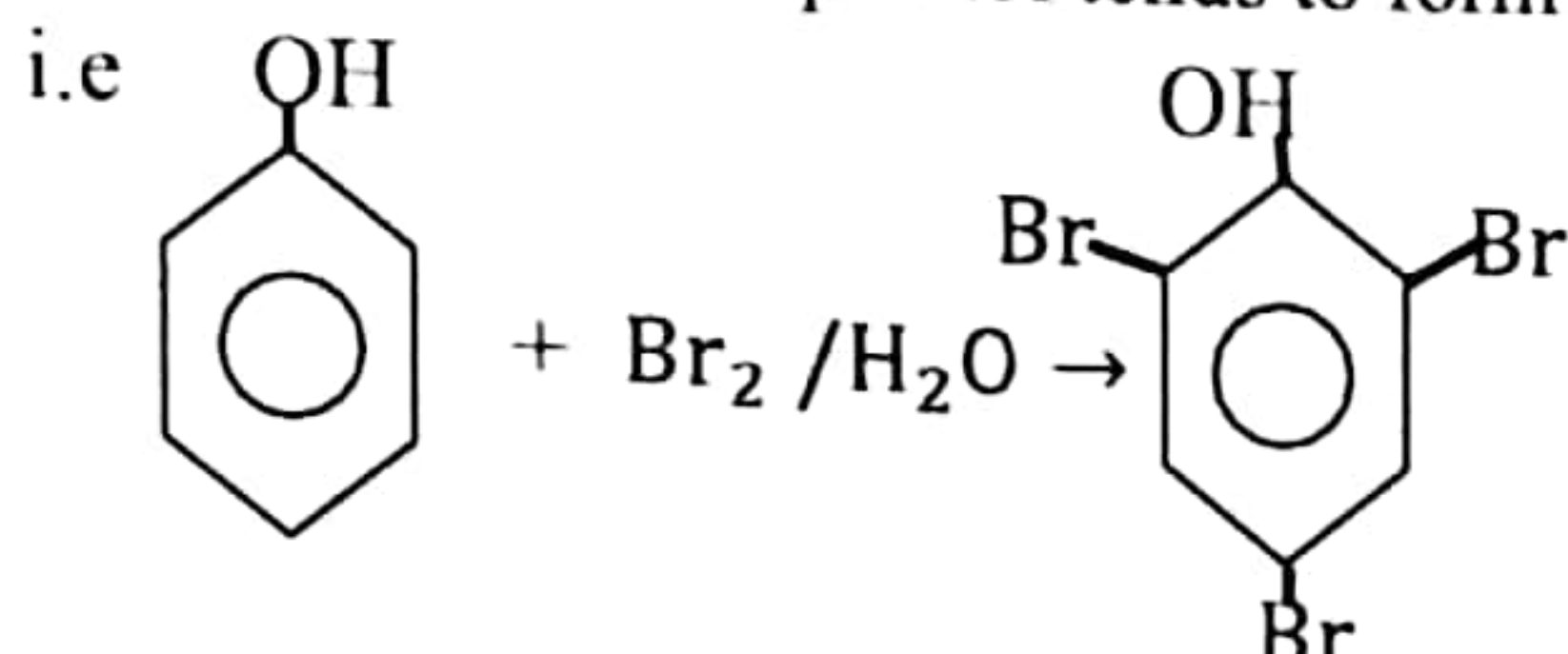
TEST OF PHENOL

- Phenol turns blue litmus paper red
- With iron (III) chloride, phenol tends to form purple / violet colouration of iron (III) phenoxide.



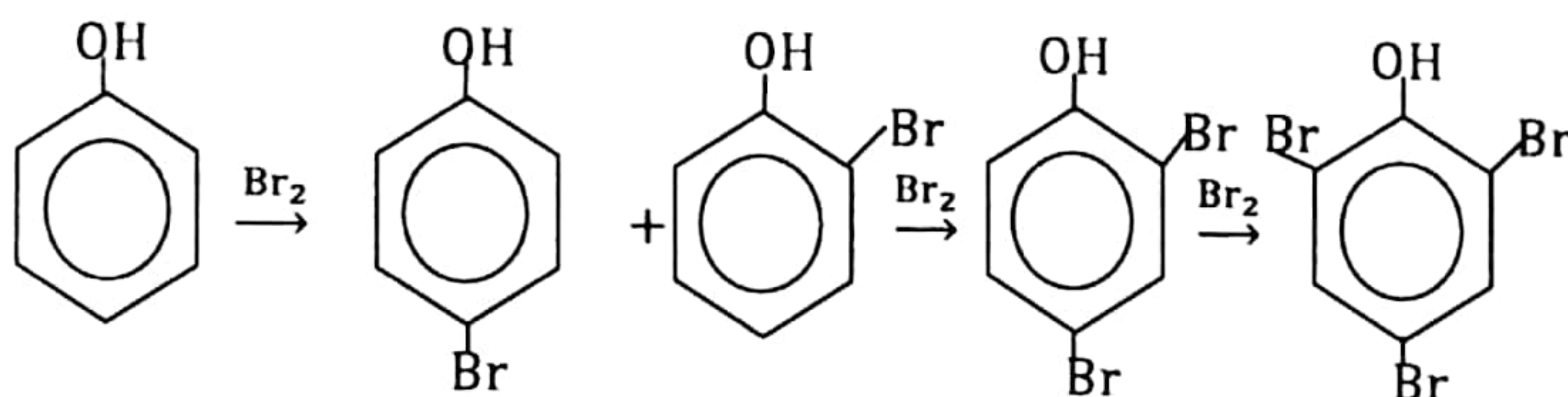
Violet complex

- With bromine water phenol tends to form white precipitate of 2, 4, 6 – tribromophenol.

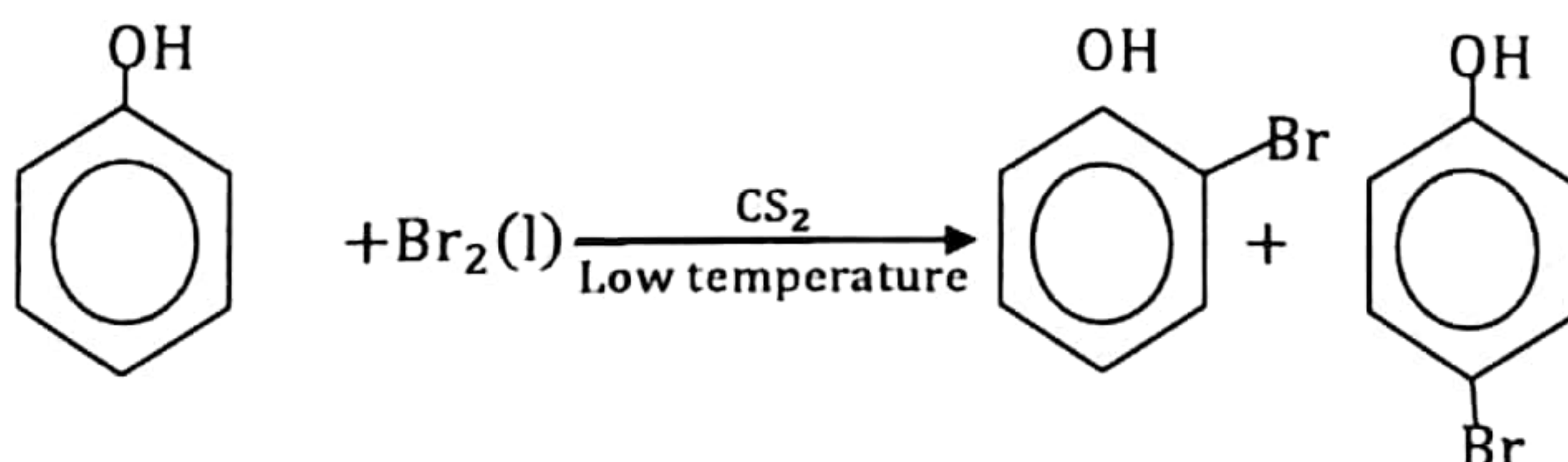


Note: Although the reaction is electrophilic substitution reaction is there no need of Lewis acid catalyst because the OH activate the benzene ring towards electrophilic substitution reaction

- The reaction takes place under influence of directing effect of OH group which is ortho –para director.



But:



(Here ortho and para products only are formed, because CS_2 being non- polar therefore does not polarise $\text{Br} - \text{Br}$ bond and deactivates electrophilic substitution reaction while polar solvent in $\text{Br}_2 \mid \text{H}_2\text{O}$ mixture cause more polarization of $\text{Br} - \text{Br}$ bond and therefore activating more electrophilic substitution reaction in benzene ring).

DIFFERENCES BETWEEN ALCOHOL AND PHENOL

Below is the summary of some differences between alcohol and phenol;

	ALCOHOL	PHENOL
1	Undergo oxidation easily (for primary and secondary alcohols)	Do not undergo oxidation easily
2	Do not react with bromine water	Form white precipitate of 2, 4, 6-tribromophenol with bromine water
3	Do not react with FeCl ₃	Form purple colouration with FeCl ₃
4	Form ester (has fruity smell) with carboxylic acid	Do not react with carboxylic acid
5	Do not react with sodium hydroxide solution	Form white precipitate of sodium phenoxide with NaOH(aq)
6	Undergo nucleophilic substitution reaction	Does not readily undergo nucleophilic substitution reaction

SIMILARITIES BETWEEN ALCOHOL AND PHENOL

- Evolve hydrogen gas with alkaline metals
- They form ether with haloalkane
- They form ester with acyl compounds (acid halide)
- They react with hydrogen halide (they can undergo halogenation)
- Both are acidic in nature (physical property)

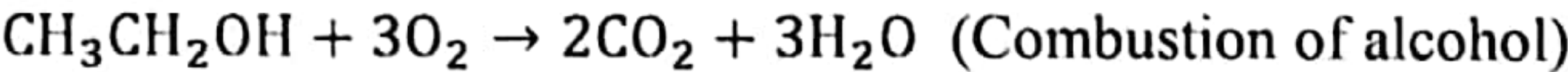
USES OF ALCOHOL

i) Drinks

Alcohol specifically ethanol is used as a drink (you should understand that the “alcohol” in alcoholic drinks is simply ethanol).

ii) As a fuel

Alcohols (particularly ethanol and methanol) burns in excess oxygen to give CO₂ and H₂O as per equation:



- The reaction is highly exothermic, and the energy evolved in the reaction can be used for useful purpose and therefore the alcohols may act as a fuel.

The ethanol (and of course methanol) may be as fuel on its own alone or in the mixture with petrol (gasoline)

- *Gasohol is the term used for fuel containing petrol-ethanol mixture.*

A main **advantage** of using ethanol as a fuel instead of petrol is that: Ethanol may be produced by the fermentation process (for example from maize which can be grown in the plants) thus making the fuel re-newable unlike petrol which is non-renewable . (In actual sense even petrol is re-newable after millions of years!)

iii) As a solvent

Alcohols (especially ethanol and propan – 2 – ol) are widely used as solvent.

- This is because they are relatively safe and can be used to dissolve many organic compounds which are insoluble in water for example as the solvent in perfumes and cosmetics.

iv) **As an industrial feedstock**

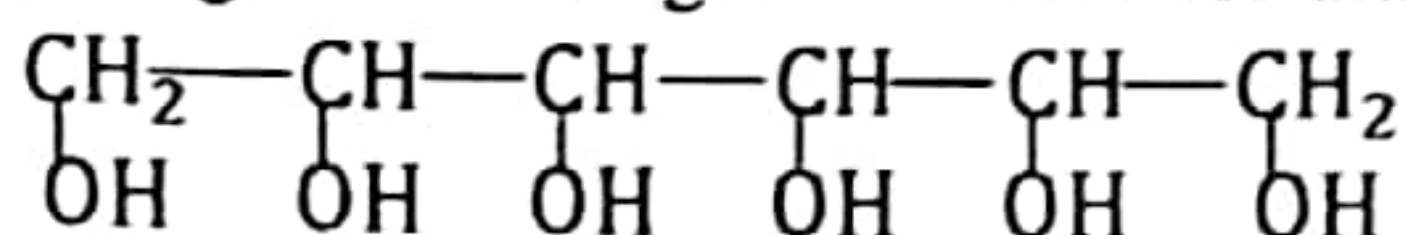
Most Alcohol (especially methanol and ethanol) are used to make other compounds.

- For example in making of aldehyde carboxylic acid and ester which in turn may be converted to other useful compounds. Also diols (especially 1,2 – ethanediol) is very useful raw material for making polyester(polymers) which has very wide applications.

v) As sugar substitute

Sorbitol (1,2,3,4,5,6 – hexanehexaol) is water soluble has a sweet test like cane sugar.

- As result, it is used in sweet making and as a sugar substitute for diabetics.



Common name: sorbitol

IUPAC name: 1,2,3,4,5,6 – hexanehexaol (hexane – 1,2,3,4,5,6 – hexaol)

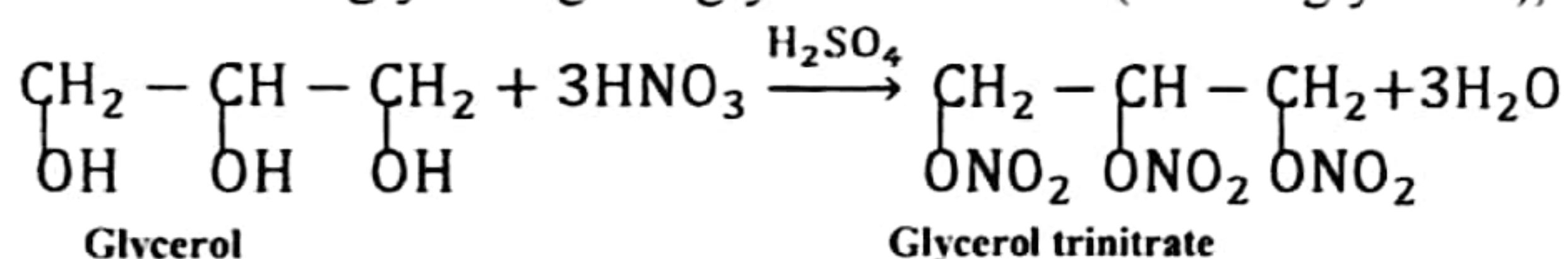
It should be noted that:

As number of OH groups increases, the alcohol becomes sweeter

vi) **In making explosives**

Glycerol (1,2,3 – propanetriol) is a syrupy, water – soluble high boiling point liquid with a sweet taste.

- Nitration of glycerol gives glycerol trinitrate (or nitroglycerine), which is used in explosives



- (Glycerol trinitrate is also used in medicine as vasodilator to prevent heart attacks in patient suffering from angina).

vii) **As anti-freezing agent.**

Alcohol (especially 1, 2 – ethanediol) is used as anti freezing agent, to lower freezing point of water.

- This is due to the strong hydrogen bonding properties of this alcohol (has two OH groups), this alcohol is miscible with water in all proportion and is highly non-volatile. So mixing it with water cause large freezing point depression (For example mixture of 60% ethane-1,2-diol and 40% water freezes at -45°C instead of 0°C which is the melting point of pure water). Besides lowering the freezing point, the antifreeze also raises the boiling point, increasing the operating range of the cooling system.



Common name: ethylene glycol

IUPAC name: 1,2 – ethanediol (or ethane – 1,2 – diol)

viii) As antiseptic

Antiseptic is the preventing the growth of disease – causing microorganism.

Ethanol is used in medical wipes and in most common antibacterial hand sanitizer gels as antiseptic (it is used in this way when its concentration is about 62%v/v)

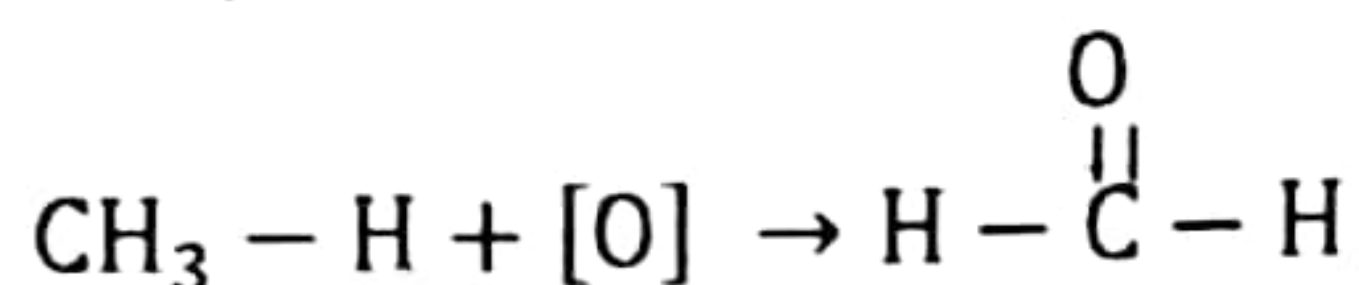
- Ethanol kills organisms by denaturing their proteins and dissolving their lipids (fatty acids). These lipids are insoluble in water but dissolve in organic solvent like alcohol.
- Alcohol is effective antiseptic against most bacteria fungi and viruses.

Hazards of alcohols

i) Blindness

Methanol is highly toxic

- It can be biochemically oxidised in the body to the methanal (formaldehyde) which cause blindness.



Where [O] stands for enzyme in the body which cause oxidation

- So methanol drinkers have very high blindness risk (even death risk).

ii) Health problem

This includes:

• Heart problem

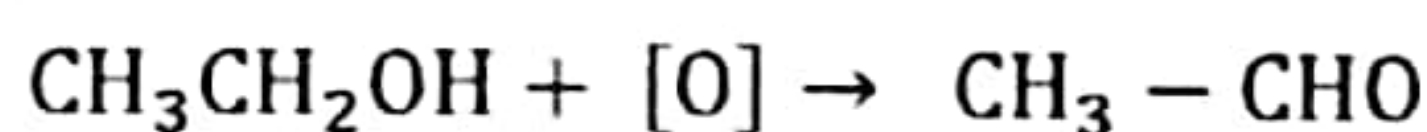
- Alcohol that is not processed by liver goes to the heart.
- The liver can process only small amount of alcohol per unit time.
- Thus when a person drinks too much alcohol, more alcohol can reach the heart reducing the force of heart contractions. As a result, the heart will pump less blood, lowering overall body blood pressure.

• Digestion problem

- Alcohol it always absorbed in small intestine where it delay the rate of absorption of nutrients.

• Physiological problems

- In the body ethanol may be biochemically oxidised to ethanal (acetaldehyde) which is more toxic than ethanol



(The oxidation is catalyzed by an enzyme known as **alcohol dehydrogenase**)

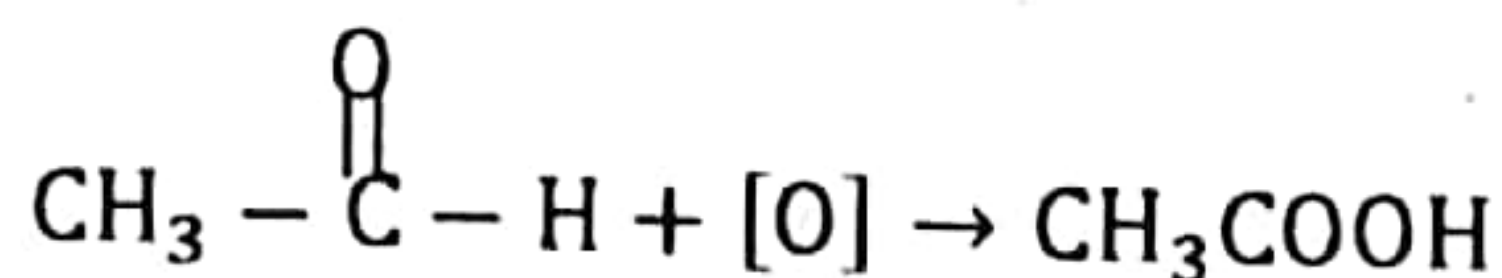
- The physiological side effects of consuming ethanol are due to the formation of the acetaldehyde. This includes:-

- Nausea
- Dizziness
- Seating
- Headaches

Therefore basically person becomes drunk because of presence of ethanal in the body.

Understand!

Under presence of another enzyme known as **aldehyde dehydrogenase**, the acetaldehyde undergoes further biochemical oxidation to give ethanoic acid; this ethanoic acid is highly toxic but it does not make person to be drunk.



(Where the oxidation is brought about by **aldehyde dehydrogenase** enzyme)

Interesting!

Some people have inactive **aldehyde dehydrogenase** and therefore these people get drunk (and other side effects of acetaldehyde) even with low consumption of alcohol (ethanol) because the aldehyde is not converted to ethanoic acid.

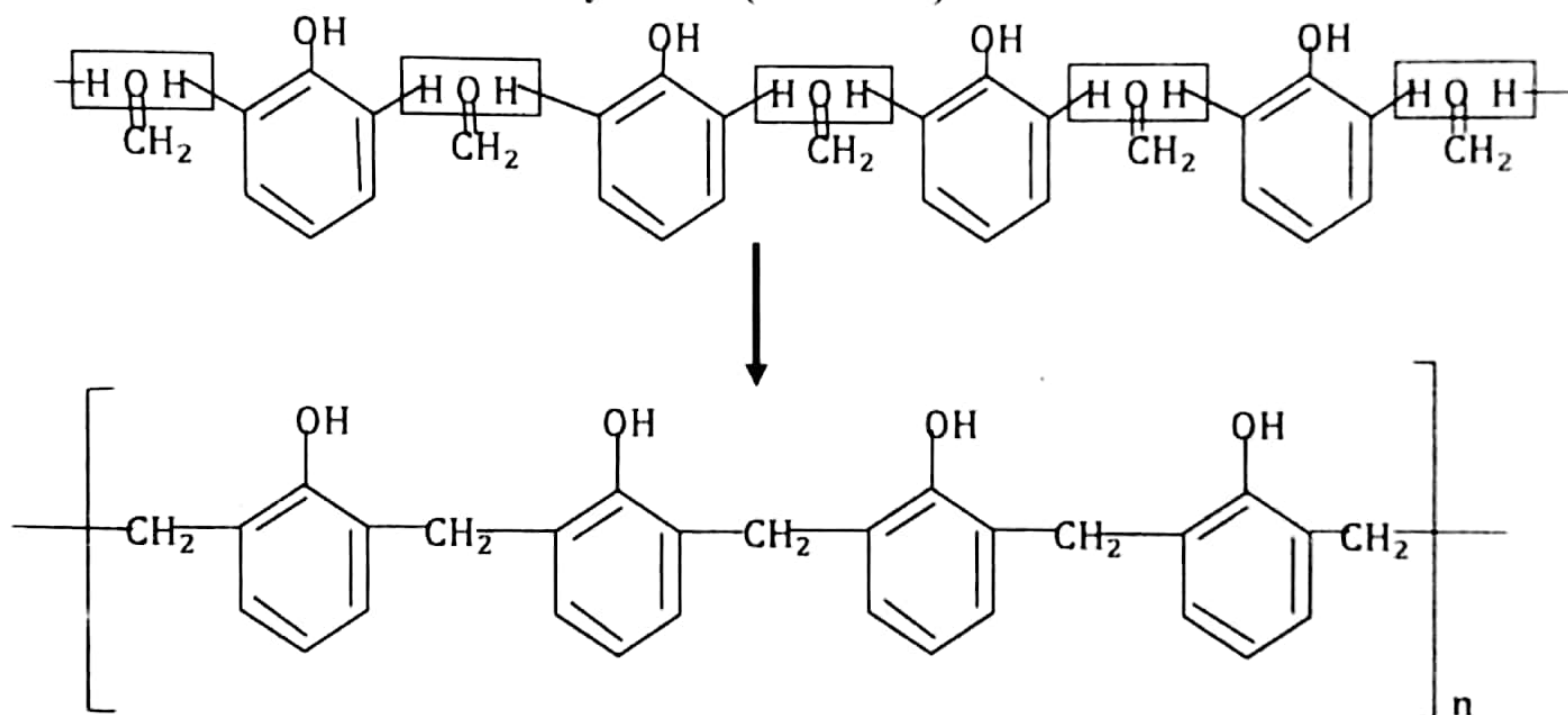
- People with very active **aldehyde dehydrogenase**, get drunk after large consumption of alcohol where the acetaldehyde become in excess to react with the aldehyde dehydrogenase enzyme.
- **Cirrhosis and cancer**
- The acetaldehyde (ethanal) formed causes cirrhosis (a chronic liver disease) and various types of cancers.
- So large and prolonged consumption of alcohols may lead to these diseases and even death

USES OF PHENOL

i) As raw material for production of plastic

This is the main use of phenol.

- When mixed with methanal phenol undergoes condensation polymerisation reaction to give a resin known as **phenol formaldehyde resin (or Bakelite)**.



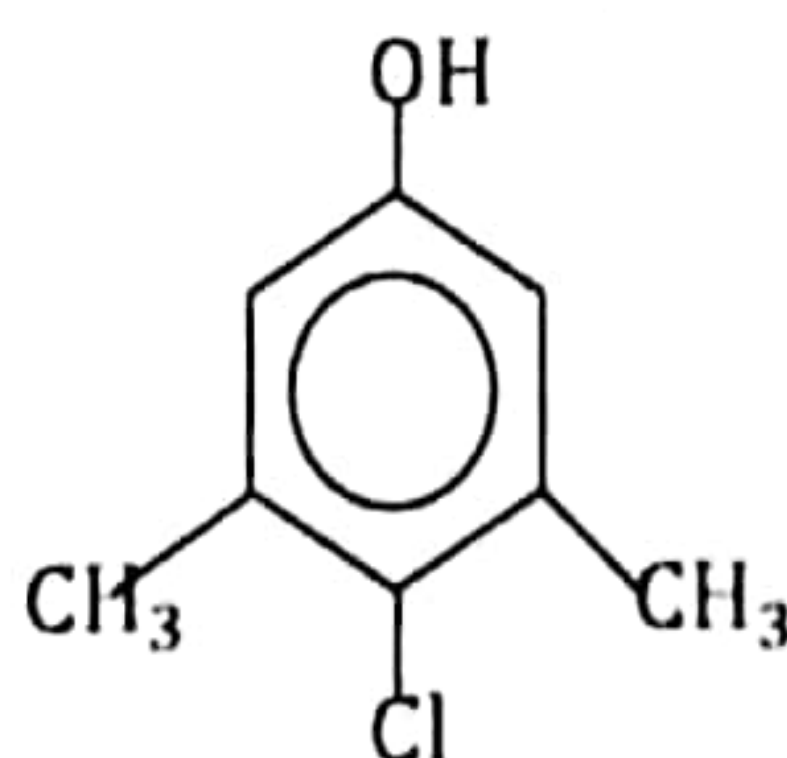
ii) As antiseptic

Dilute solutions of phenols are good disinfectants and therefore phenols can be used as antiseptics.

However....!

Phenol is toxic and can cause burn to the skin; so only less toxic phenols are used to make antiseptic.

- In most cases these antiseptics are chlorinated phenols for example **dettol**.

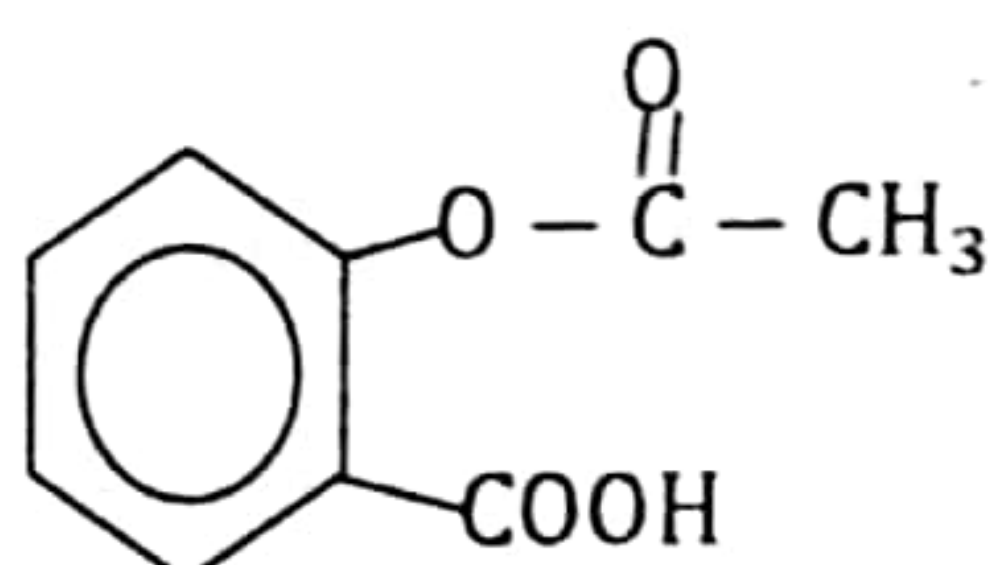


Common name: Dettol

IUPAC name: 4-chloro-3,5-dimethylphenol

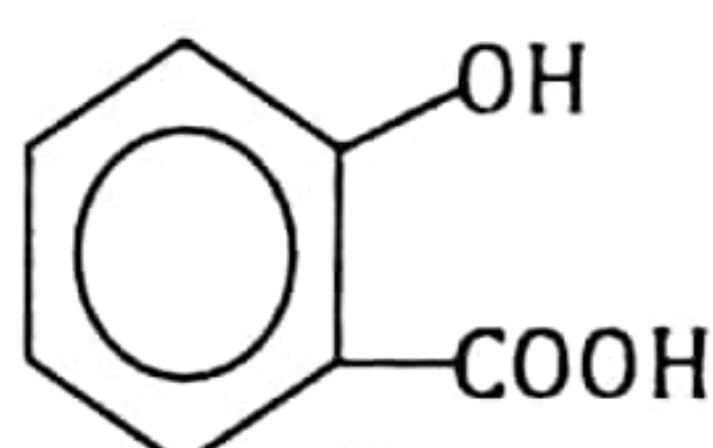
iii) As raw material in production of herbicides and pharmaceutical drugs

- Many drugs contain phenol derivatives directly or are produced from phenol itself and its derivative. A good example of this is aspirin.



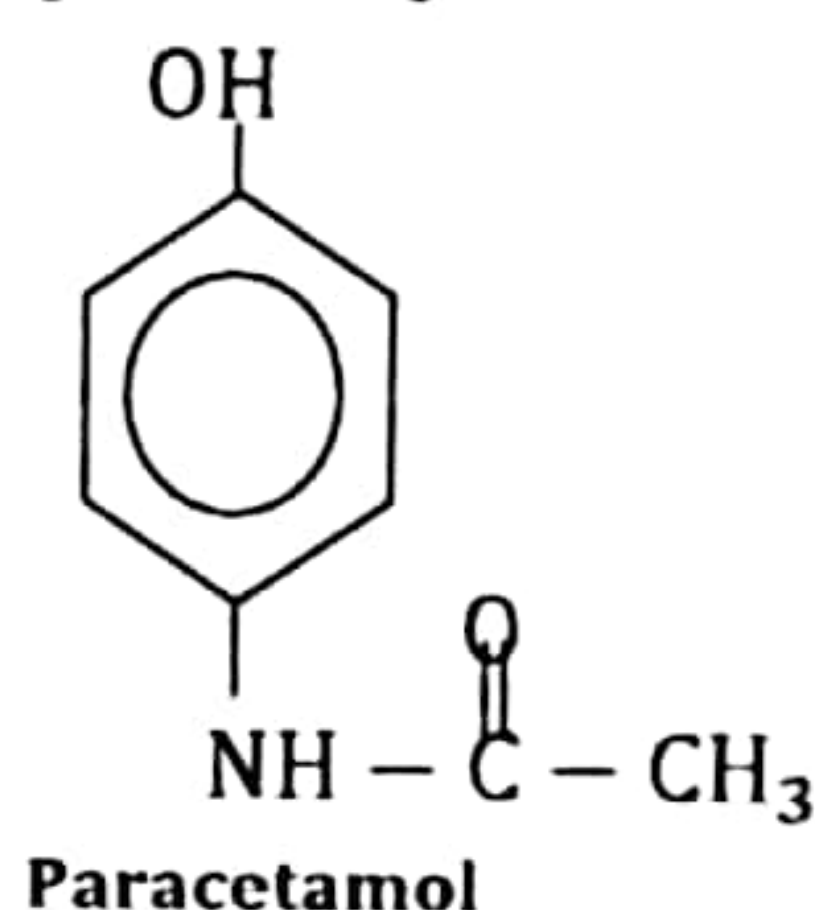
Aspirin

Aspirin is produced from salicylic acid which has the following formula (with phenol group)



salicylic acid

Another common example of drug made from phenol is paracetamol with the following formula



Paracetamol

HAZARDS OF PHENOLS

i) **Blindness**

Contact with phenol liquid or vapour cause severe burn and possible irreversible eye damage; that is permanent blindness.

ii) **Skin damage**

Direct skin contact to phenols may result into white, wrinkled discolouration, followed by severe burn (However on initial contact little or no pain may be felt).

iii) **Digestive tract damage**

This problem arises when phenol is swallowed.

- Indigestion of phenol may cause severe and permanent damage to the digestive tract by causing perforation of the tract.

iv) **Liver and kidney damage**

This problem arise due to;-

- Indigestion of phenol
- Inhalation of phenol vapour
- Prolonged exposure to phenol

Either of the above may lead to serious damage of liver and kidney.

v) **Respiratory system problem**

This may result from either swallowing (indigestion) or inhalation of phenol.

It may lead to respiratory failure and hence death

vi) **Nervous system problem**

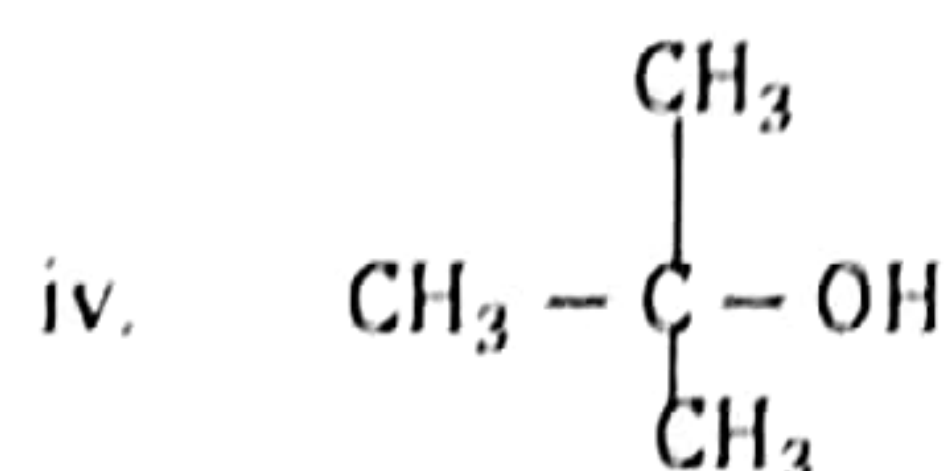
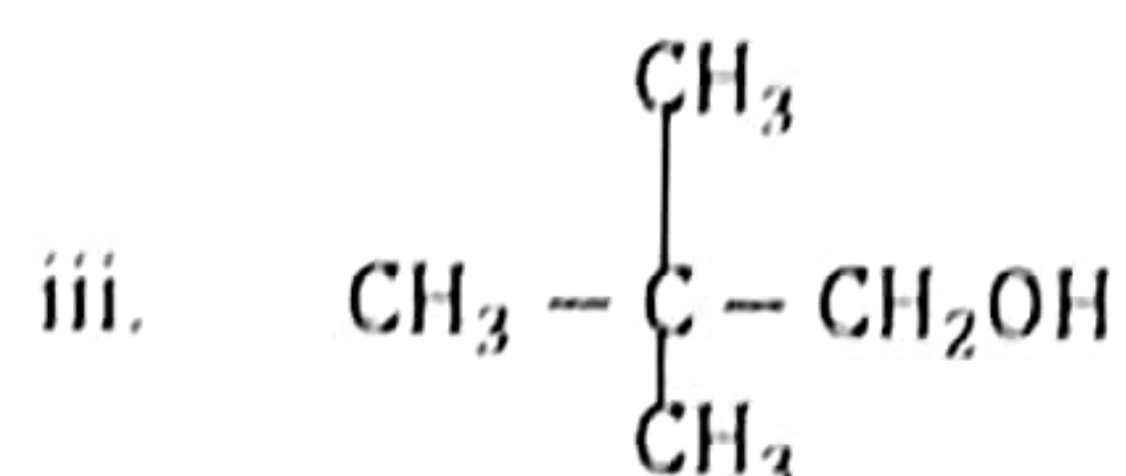
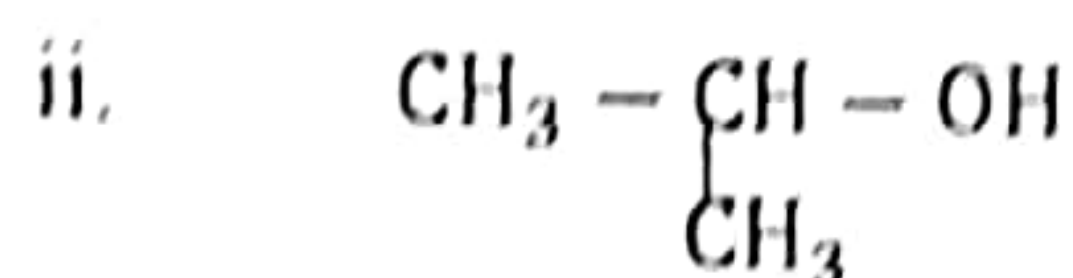
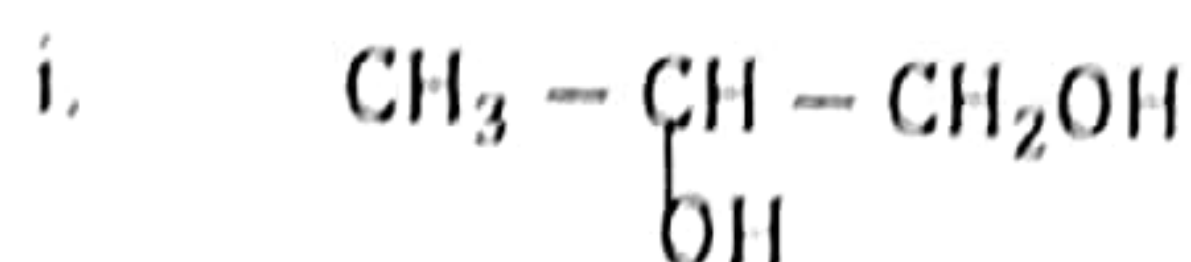
Either swallowing of phenol liquid or inhalation of phenol vapour may result to this problem.

- Swallowing of the liquid may cause central nervous system depression, characterized by excitement, followed by headache dizziness, drowsiness and nausea. Advanced stages may cause collapse, unconsciousness and eventually death.
- Inhalation of the phenol vapour cause pallor, loss of appetite, nausea, vomiting, diarrhea, weakness, darkened urine, headache, sweating, unconsciousness, fatigue, pulmonary edema and coma.

PRACTICE EXERCISE 18

Problem 1

Classify the following alcohols as primary, secondary or tertiary.



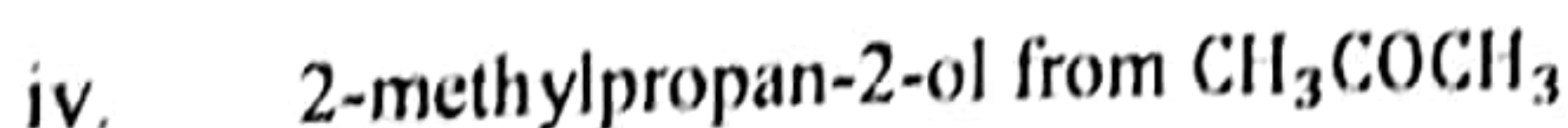
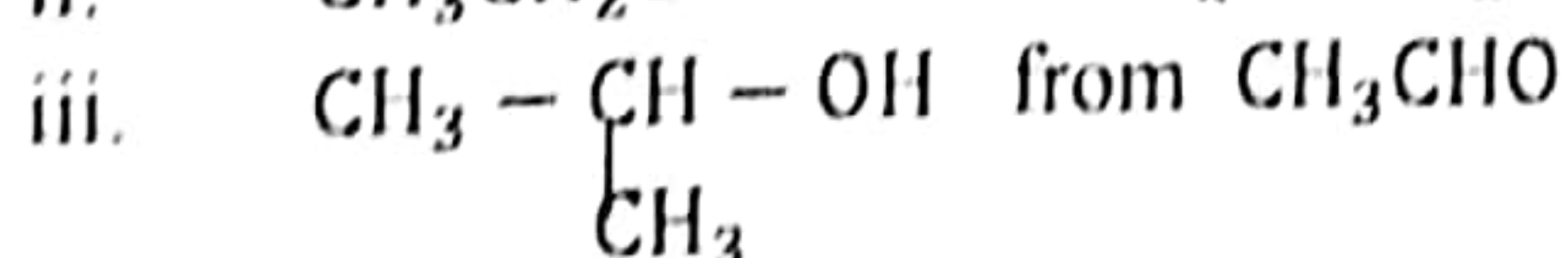
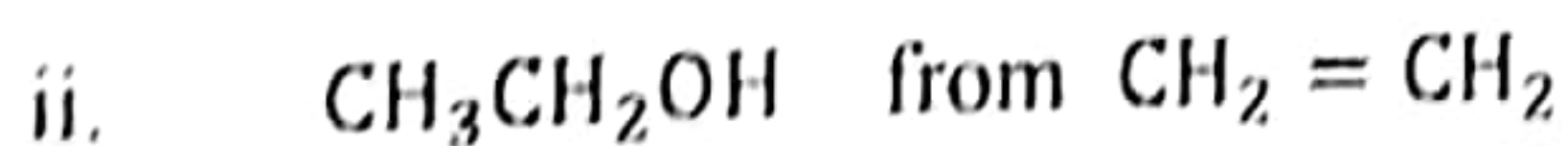
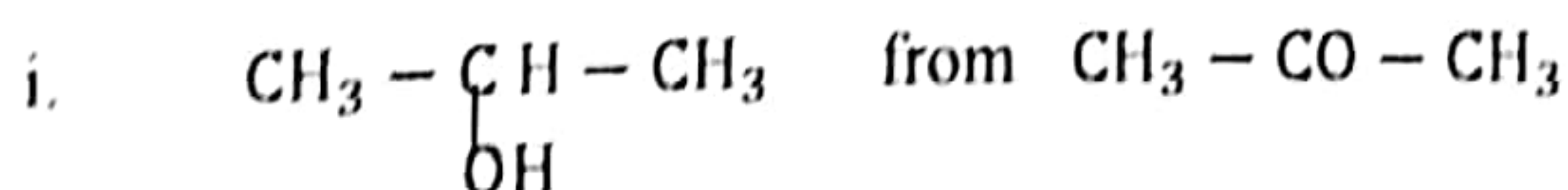
Problem 2

Write structures and give trivial names of the following:-

- i. Ethenol
- ii. Ethanol
- iii. Propan-2-ol
- iv. 1,2-ethanediol
- v. 1,2,3,4,5,6-hexanehexaol
- vi. 4-chloro-3,5-dimethylphenol

Problem 3

Write down chemical equation to show preparation of:

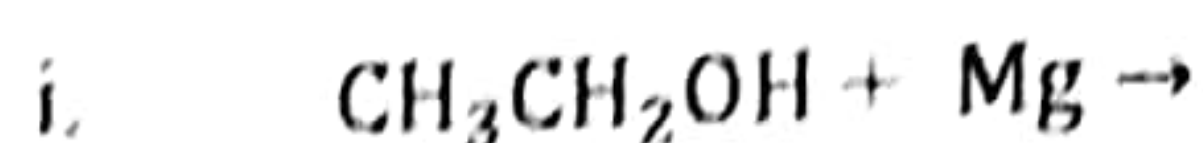


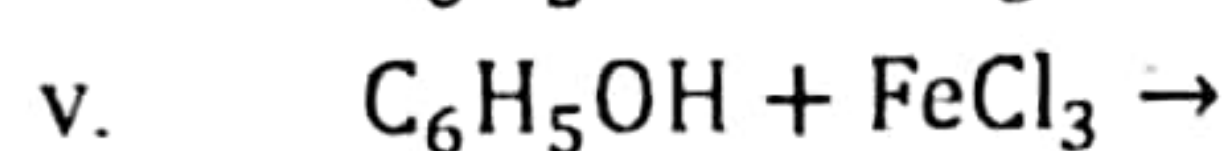
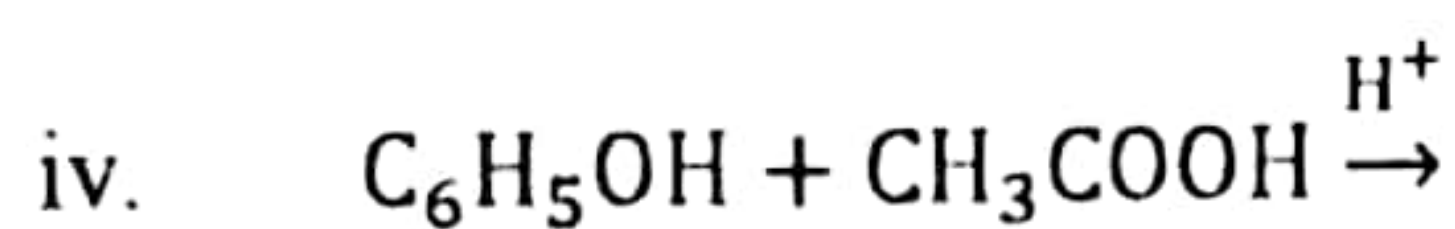
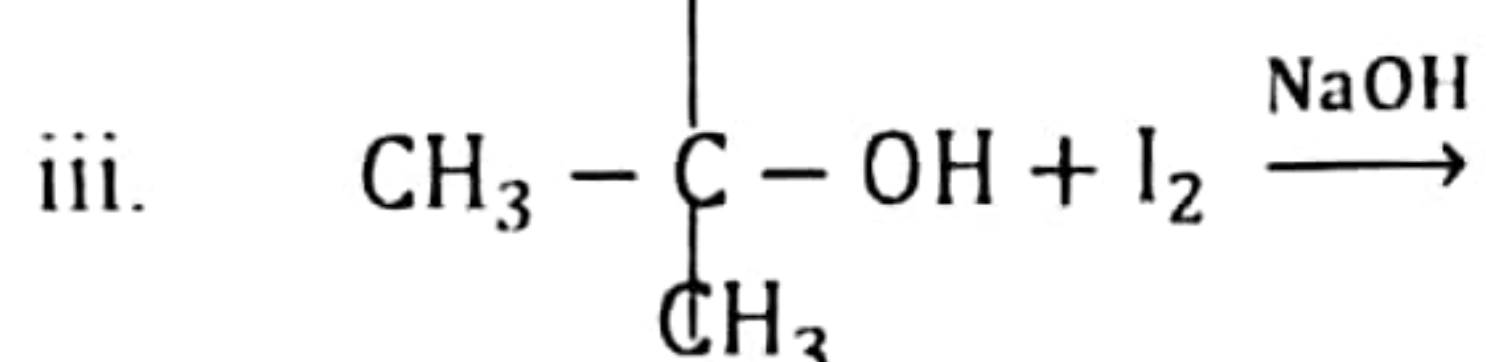
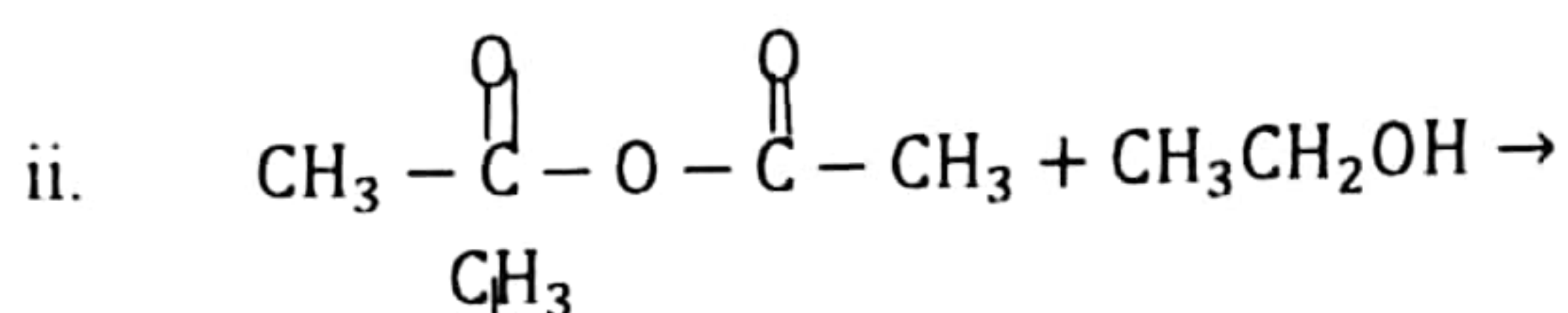
Problem 4

Explain clearly how ethanol can be produced from molasses by fermentation.

Problem 5

Complete the following organic reactions:



**Problem 6**

List down

- a. At least three uses of:
 - i. Alcohol
 - ii. Phenol
- b. At least three hazards of:
 - i. Alcohol
 - ii. Phenol

Chapter 19

CARBONYL COMPOUNDS**INTRODUCTION**

Carbonyl compounds are organic compounds with carbonyl group (>C=O) as functional group.

- If the carbonyl group is directly bonded to two alkyl groups or two aryl group or one alkyl group and one aryl group the resulting carbonyl compound is known as **ketone**.

i.e. General structure of ketone can be represented as $\text{R} - \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{R}'$ Where R and R' can be alkyl or aryl group.

- If the carbonyl compound is directly bonded to at least one hydrogen atom the resulting carbonyl compound is known as **aldehyde**.

i.e. General structure of aldehyde is $\text{R} - \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{H}$ where R can be alkyl group, aryl group or hydrogen atom.

In writing condensed formula of aldehyde, group, the aldehyde group is always written as -CHO and not -COH that could not be easily confused with alcohol. For example ethanal is commonly written as CH_3CHO .

- Both aldehydes and ketones (carbonyl compounds) have general molecular formula of $\text{C}_n\text{H}_{2n}\text{O}$, thus aldehydes and ketone are isomeric (they exhibit position isomerism).
- Most of the properties of aldehyde are the same as those of ketones because they have the same functional group but there are some differences due in their structures.

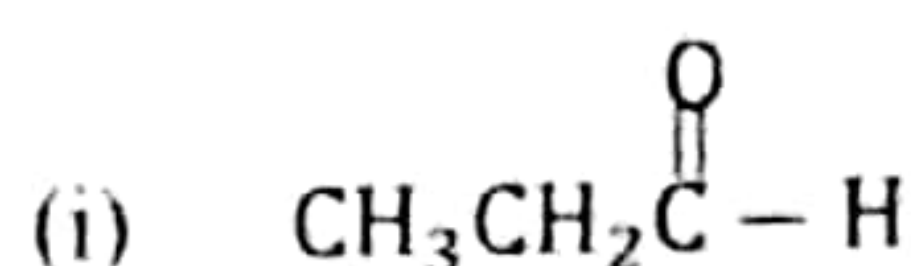
NOMENCLATURE OF CARBONYL COMPOUNDS

Rules of naming carbonyl compounds are the same as those of naming alkanes with the following modifications:

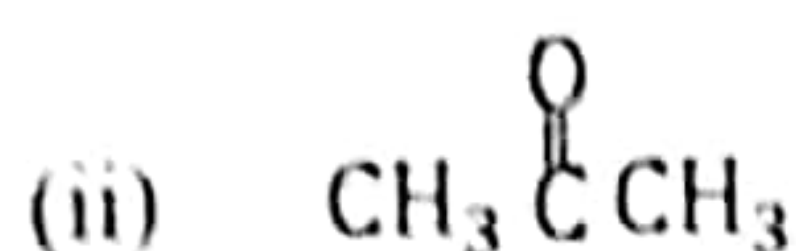
- The parent chain must contain carbonyl group, i.e. The parent chain is the longest continuous carbon chain with carbonyl group
- Numbering of carbons is done as follows
 - For aldehyde the carbon in carbonyl group must be given first position
 - For ketone numbering must start at the end closer to carbonyl group
- For ketone with more than four carbons position of carbonyl group must be indicated by using arabic numerals
- In naming aldehyde leave the suffix 'e' from the name of corresponding hydrocarbon and end with suffix -al and for ketone leave the suffix 'e' from the name of corresponding hydrocarbon and then end with suffix -one .

Example 1

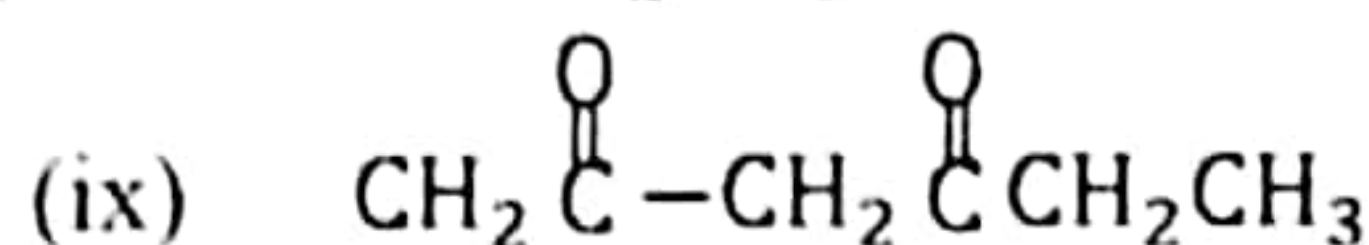
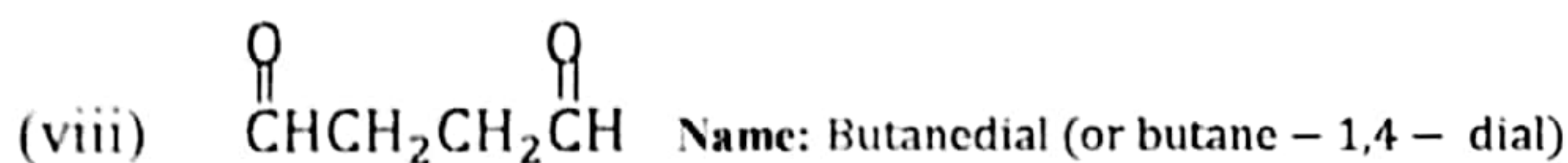
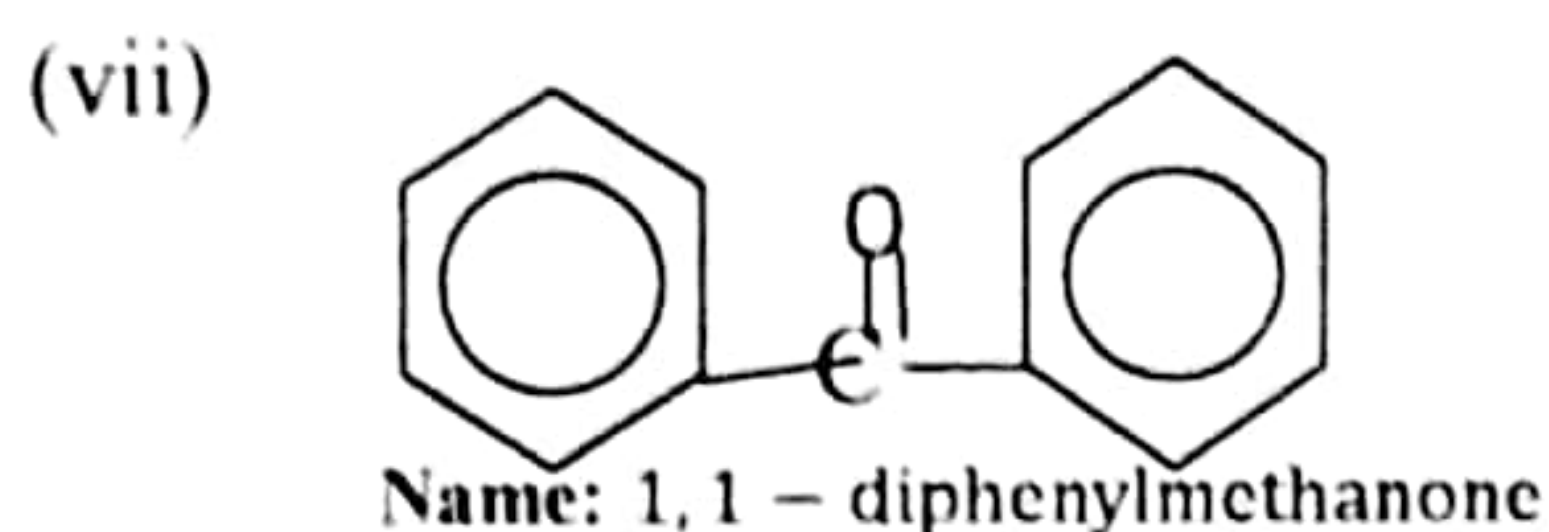
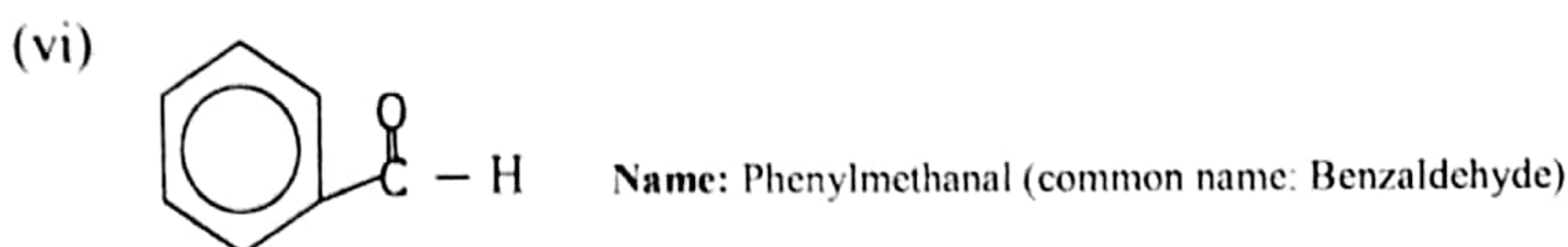
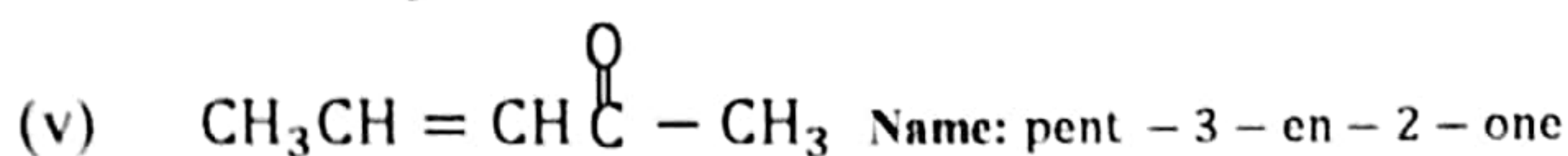
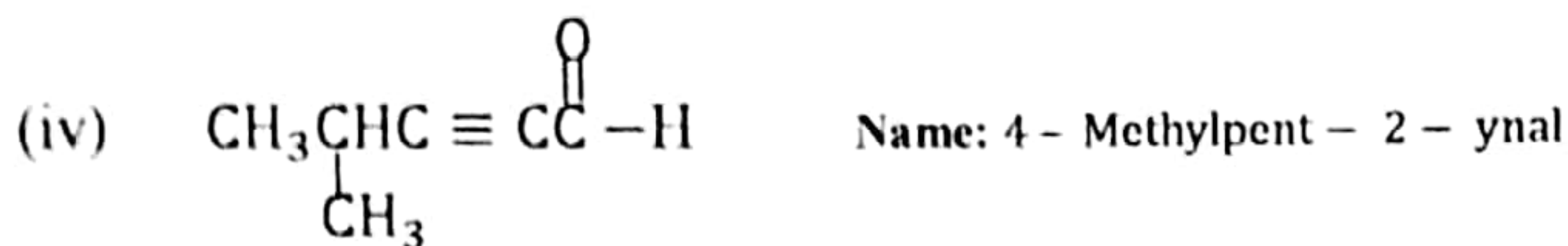
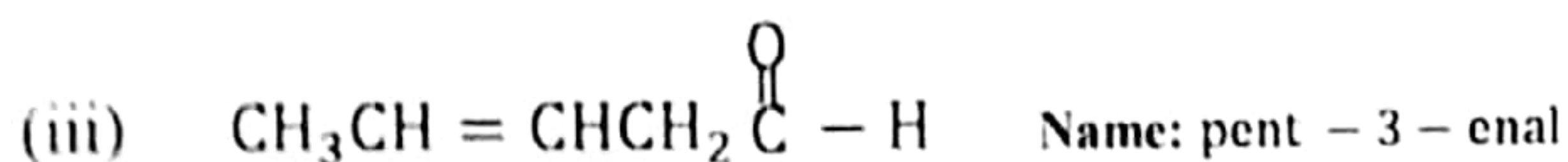
Name the following organic compounds:



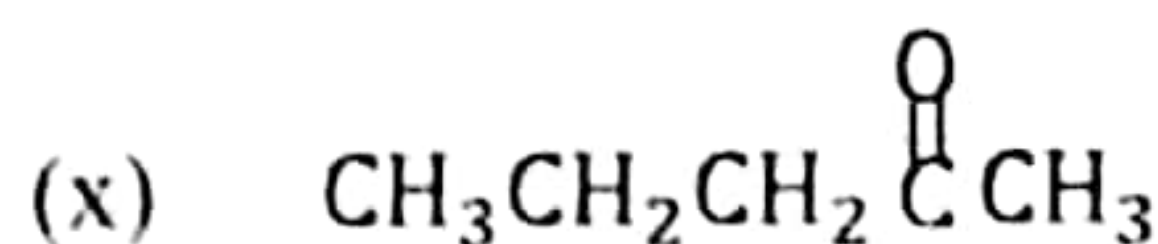
Name: Propanal



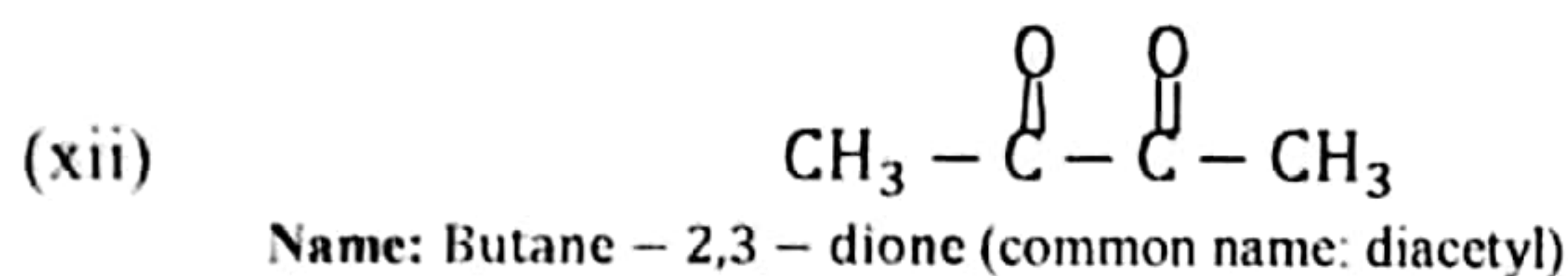
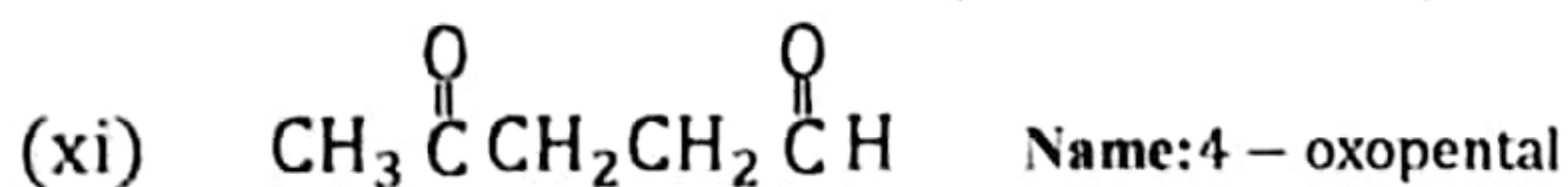
Name: propanone



Name: hexane - 2,4 - dione (or 2,4 - hexanedione)



Name: Pentan - 2 - one (or 2 - Pentanone)

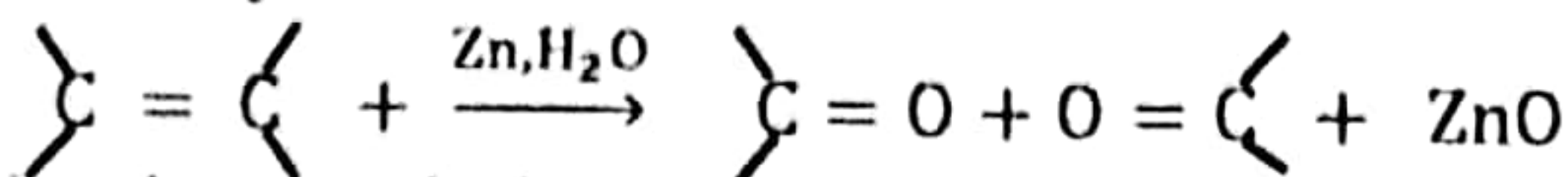


PREPARATIONS OF CARBONYL COMPOUNDS

a) Ozonolysis followed by reductive hydrolysis of alkenes

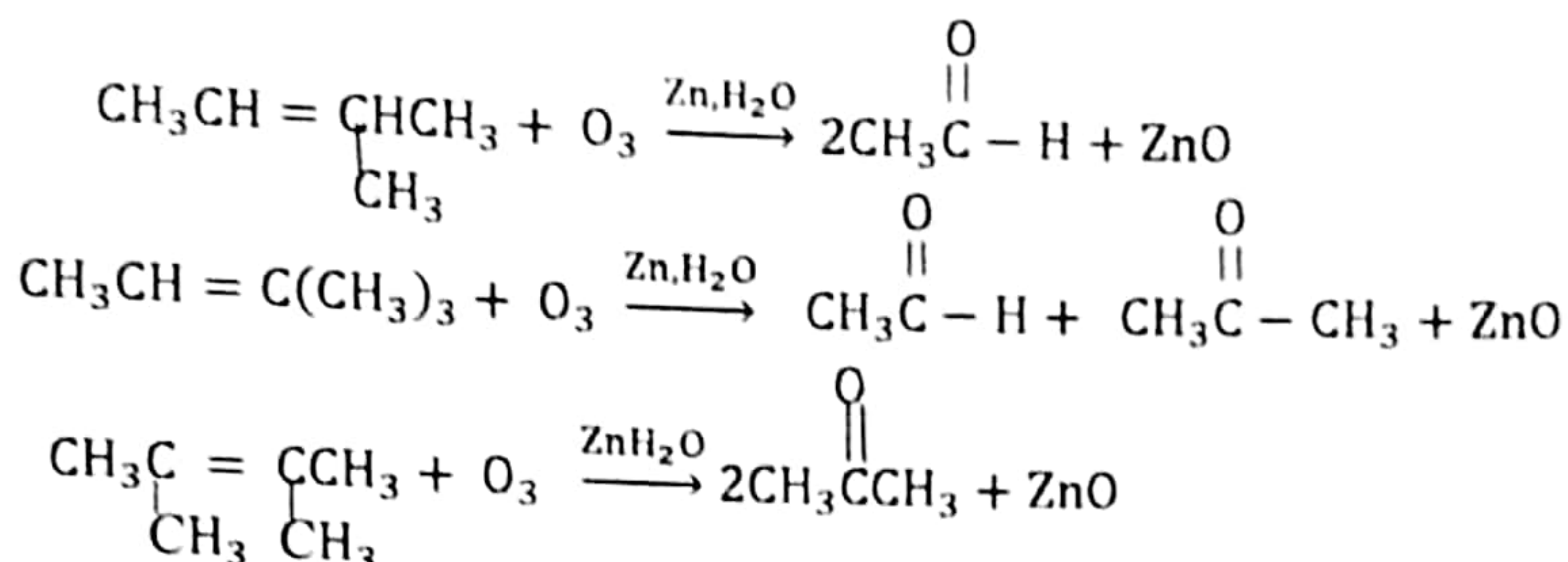
Alkene reacts with ozone followed by reductive hydrolysis done by zinc under presence of water yielding carbonyl compounds.

Generally:



If there is at least one hydrogen atom carbon with double bond aldehyde is formed and if there is no H at the carbon with double bond ketone is formed.

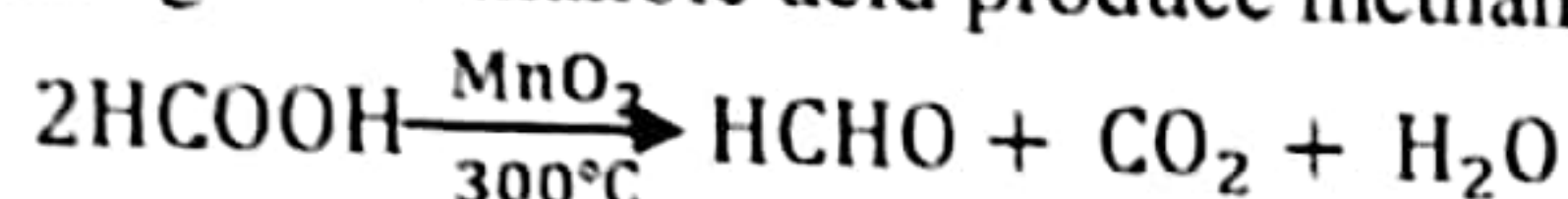
Examples:



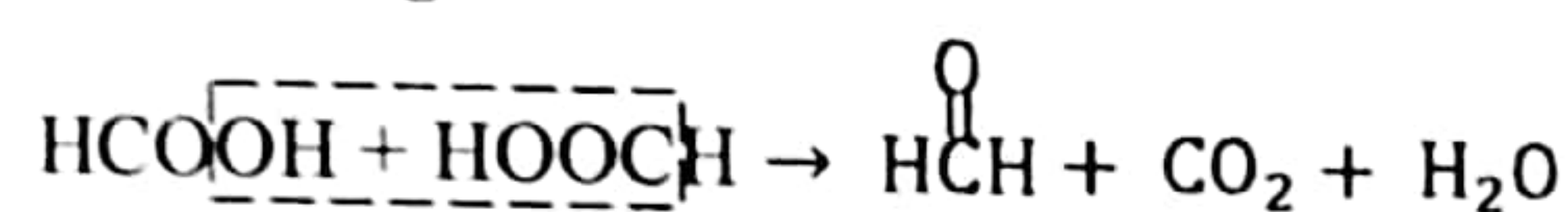
b) Heating carboxylic acids

When carboxylic acid is heated to a temperature of about 300°C under presence of manganese (iv) oxide (MnO₂), carbonyl compounds are formed.

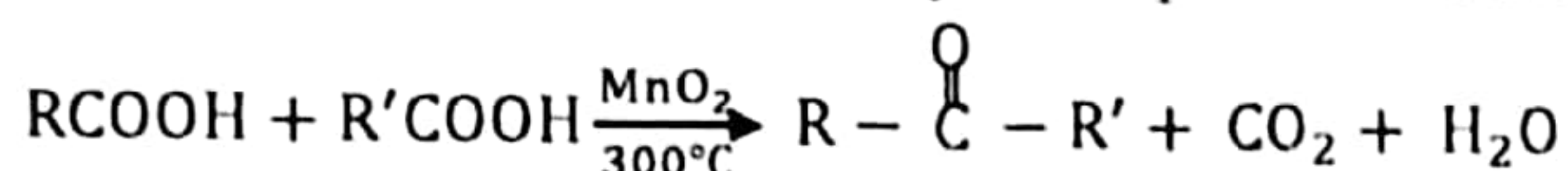
– Heating of methanoic acid produce methanal (aldehyde)



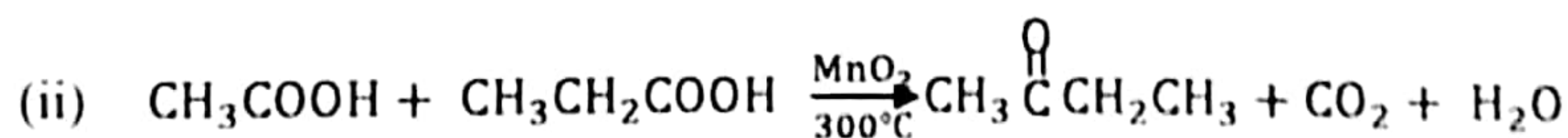
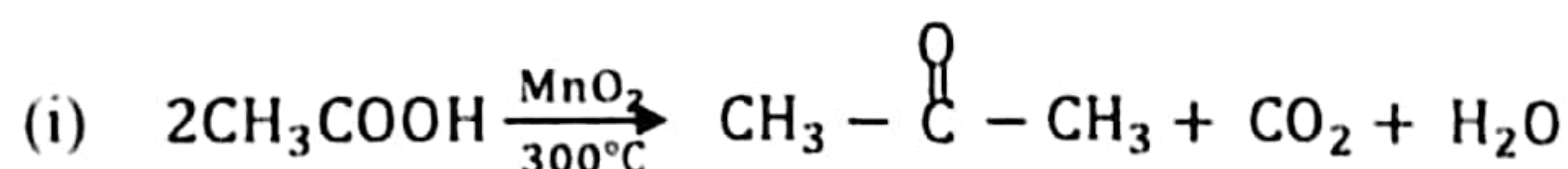
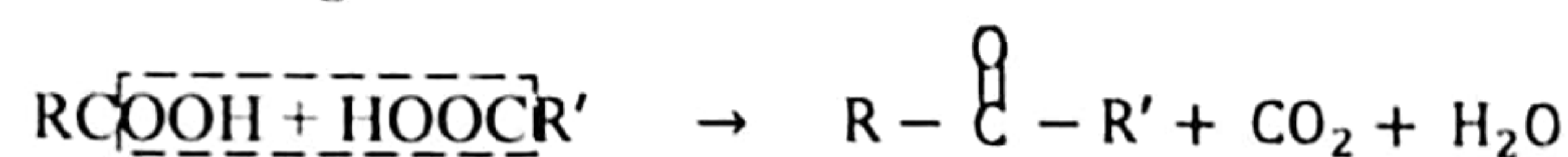
Memorising



i) Heating higher members of carboxylic acid produce ketones



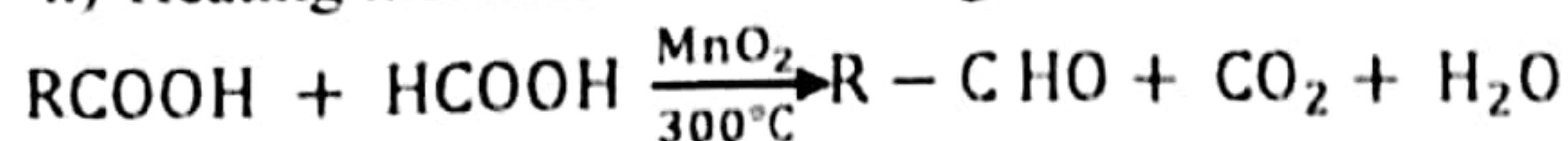
Memorising:



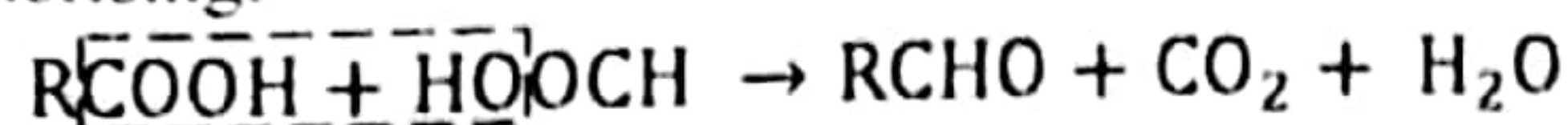
Memorising:



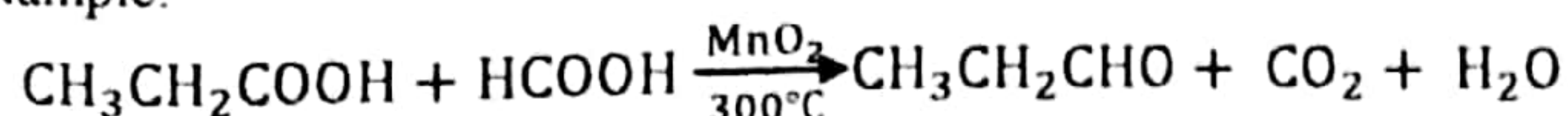
ii) Heating methanoic acid and higher member of carboxylic acid produce aldehyde



Memorising:



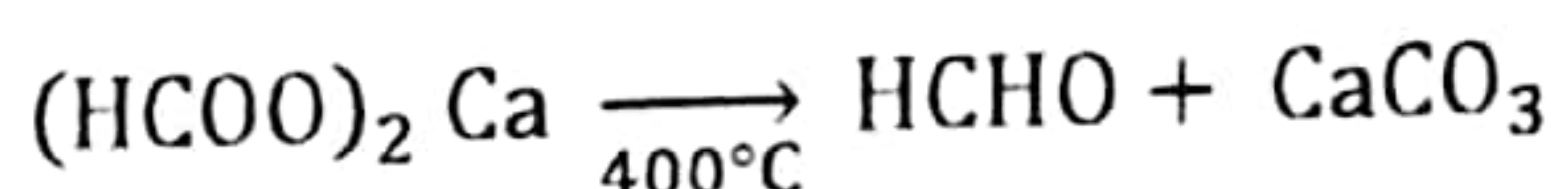
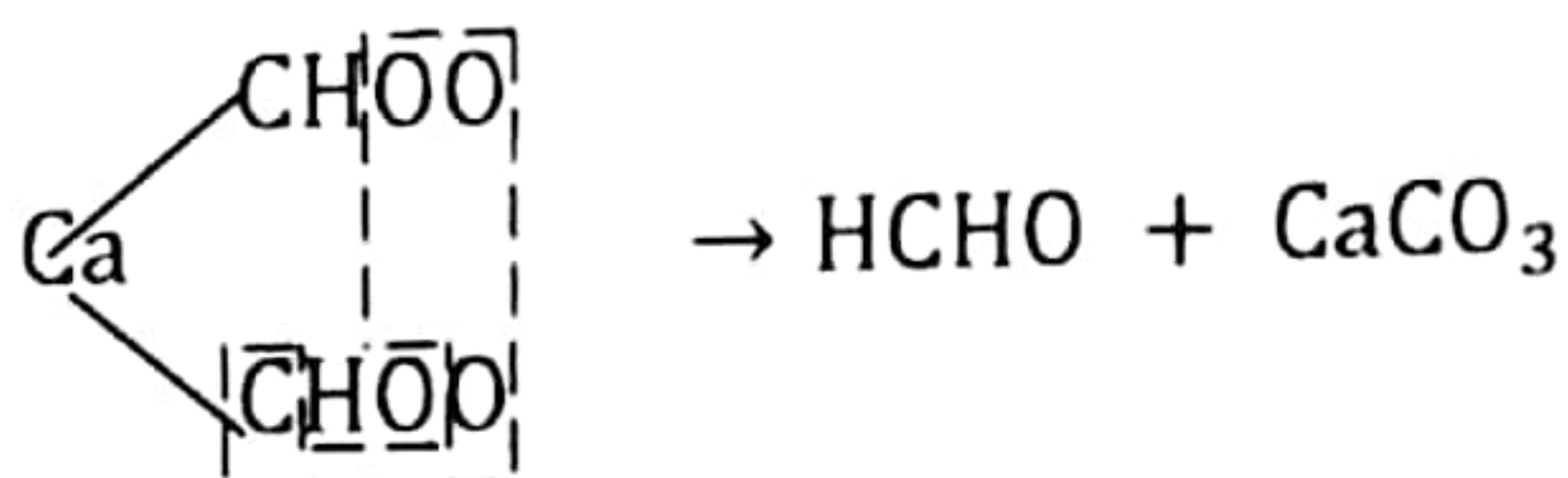
Example:



c) Heating of calcium carboxylates

When calcium carboxylates are heated to temperature of about 400°C, carbonyl compounds are formed.

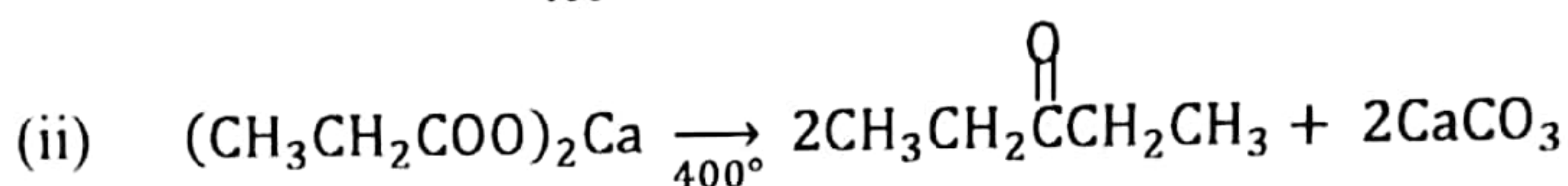
Heating calcium methanoate produce methanal.

**Memorising**

- Heating higher members of calcium carboxylates produce ketones i.e.

$$(\text{RCOO})_2\text{Ca} + (\text{R}'\text{COO})_2\text{Ca} \xrightarrow{400^\circ\text{C}} 2\text{R} - \text{CO} - \text{R}' + 2\text{CaCO}_3$$

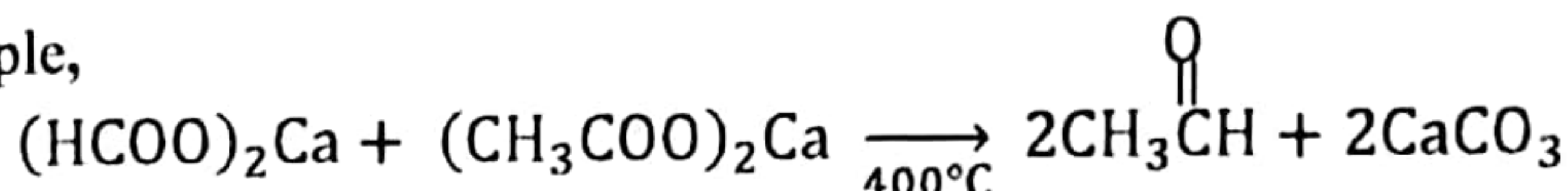
Examples:



- Heating calcium methanoate and higher member of calcium carboxylates produce aldehydes

$$(\text{HCOO})_2\text{Ca} + (\text{RCOO})_2\text{Ca} \xrightarrow{400^\circ\text{C}} 2\text{R} - \text{CO} - \text{H} + 2\text{CaCO}_3$$

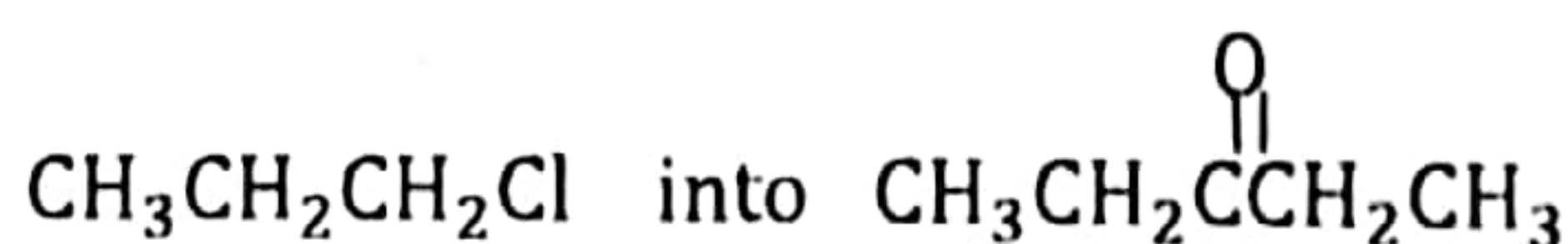
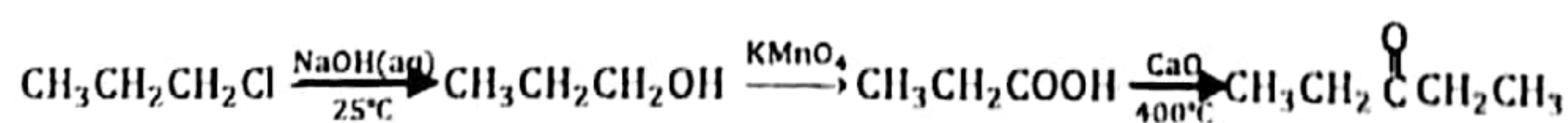
Example,

**You should notice that:**

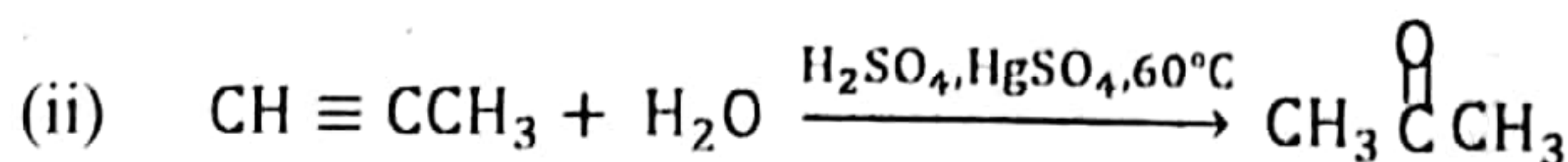
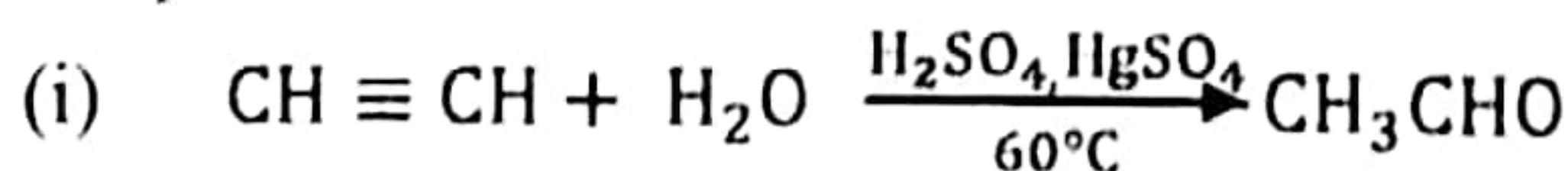
Reactions (b) and (c) in above preparations show an increase number of carbons from n to $2n - 1$ in the case of which the same type of acid applied so reactions are very useful in dealing with conversion problems which show that number of carbons has been increased from n to $2n - 1$

Example 2

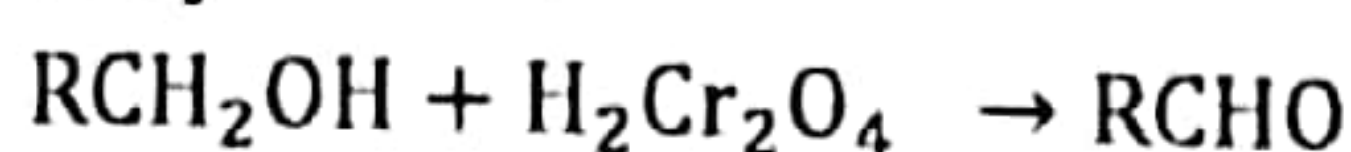
Show how would you convert

**Solution**

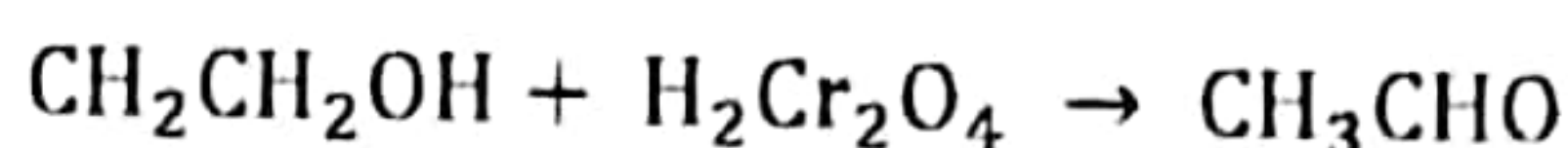
- d) Hydrolysis of alkyne under presence of concentrated sulphuric acid and mercury sulphate
 Examples:

**e) Oxidation of alcohols**

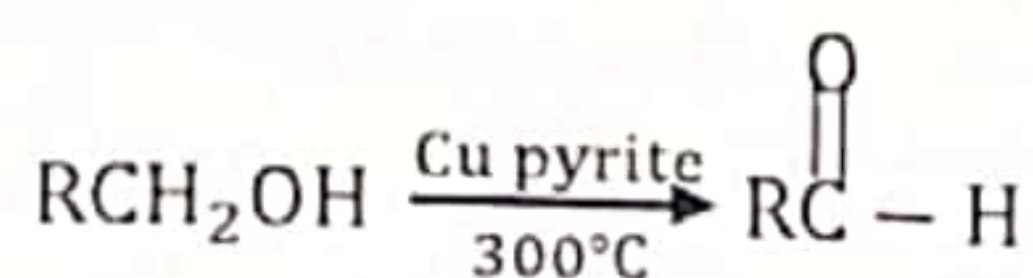
Primary alcohols gives aldehydes and the oxidizing agent must be weak like $\text{H}_2\text{Cr}_2\text{O}_4$ to prevent further oxidation of aldehyde to carboxylic acid.



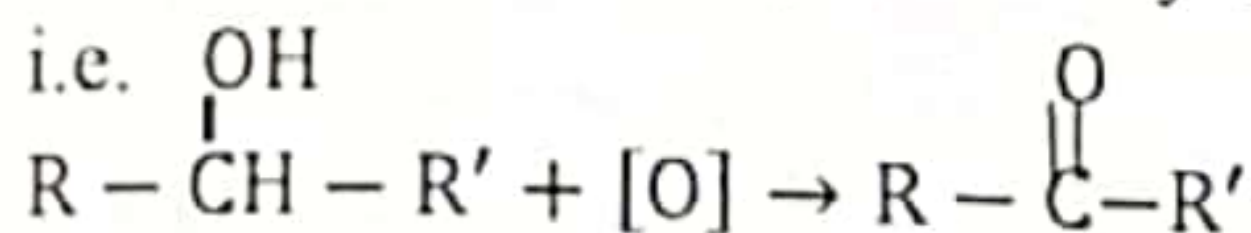
Example,



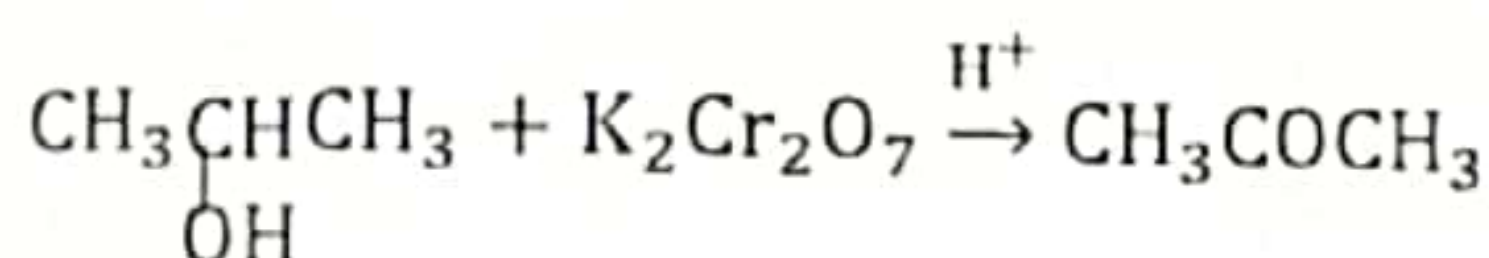
- The more appropriate method of preparing aldehyde which ensures higher yield percentage of formation of aldehyde rather than carboxylic acid is heating alcohol under presence of copper pyrites catalyst.



Oxidation of secondary alcohols yields ketones.

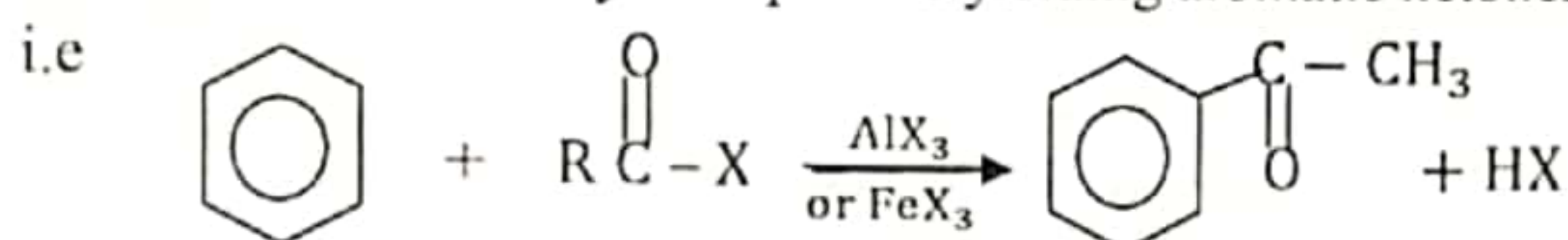


Example,

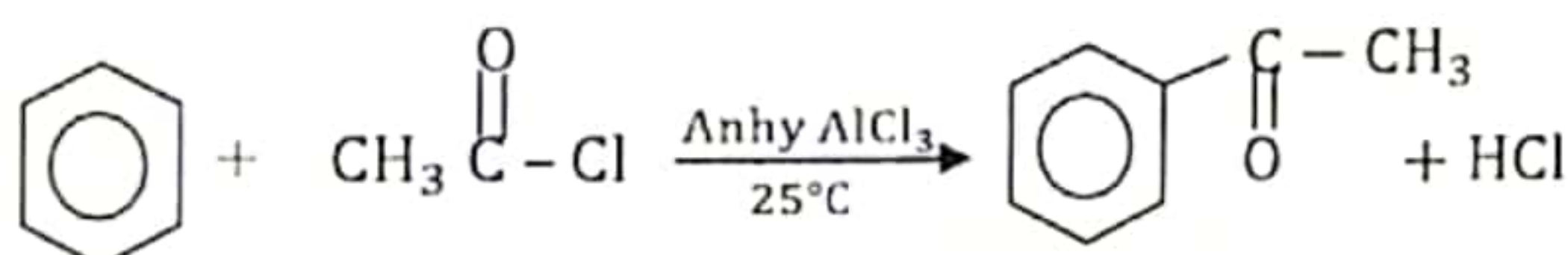


f) Friedel Craft acylation

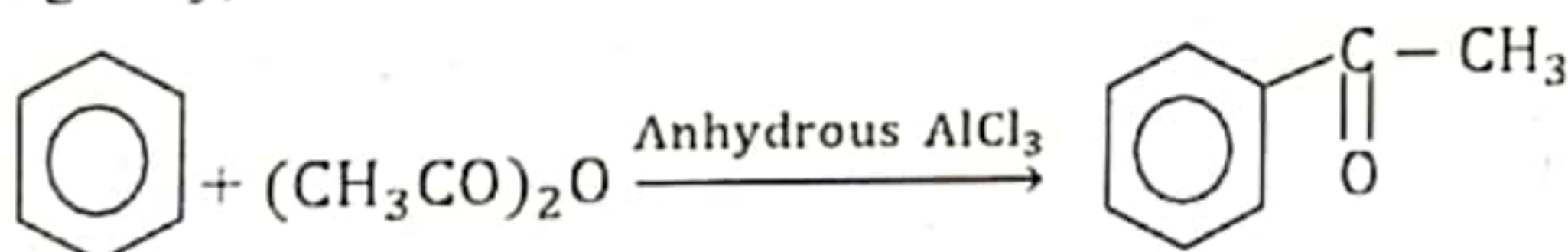
Benzene reacts with acyl compounds yielding aromatic ketones



Example,



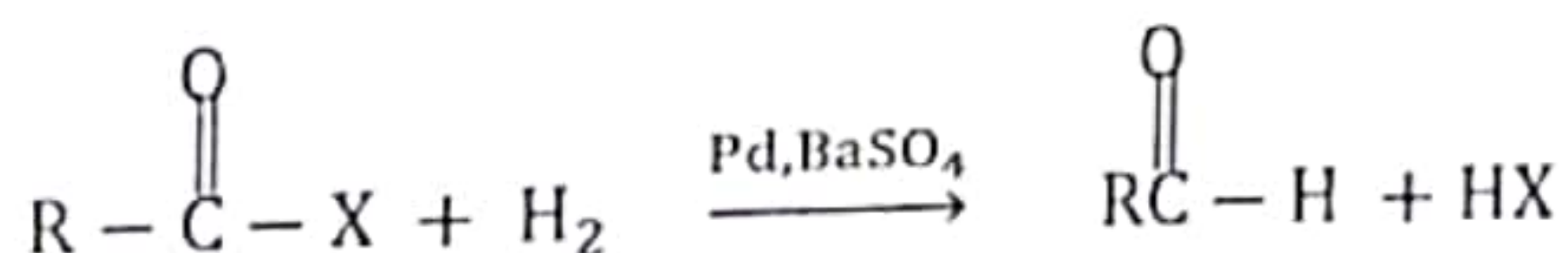
Analogously;



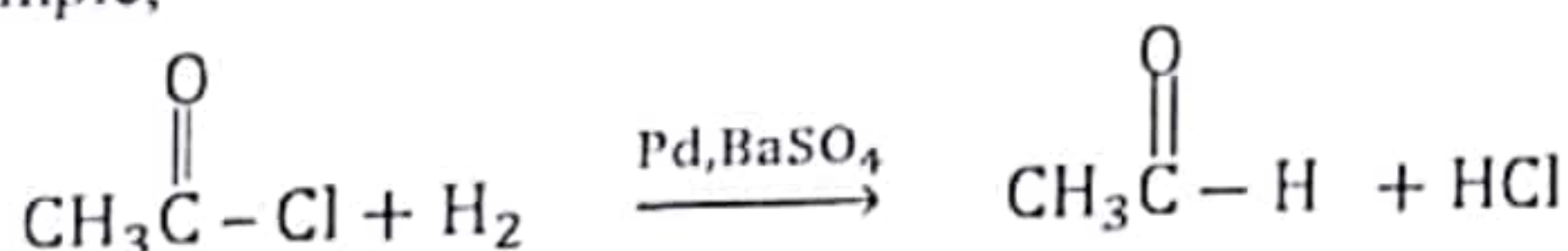
g) Reduction of acyl compounds (Rosenmund reaction)

Acyl compounds react with hydrogen gas under presence of palladium catalyst poisoned with sulphur containing compounds (mainly BaSO_4 is used) to form aldehyde.

i.e

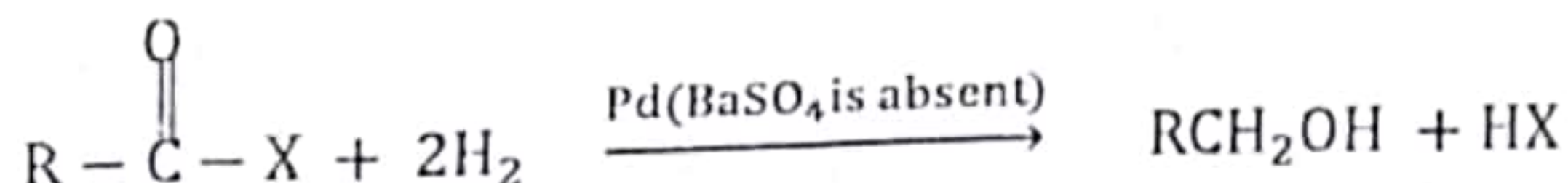


Example,



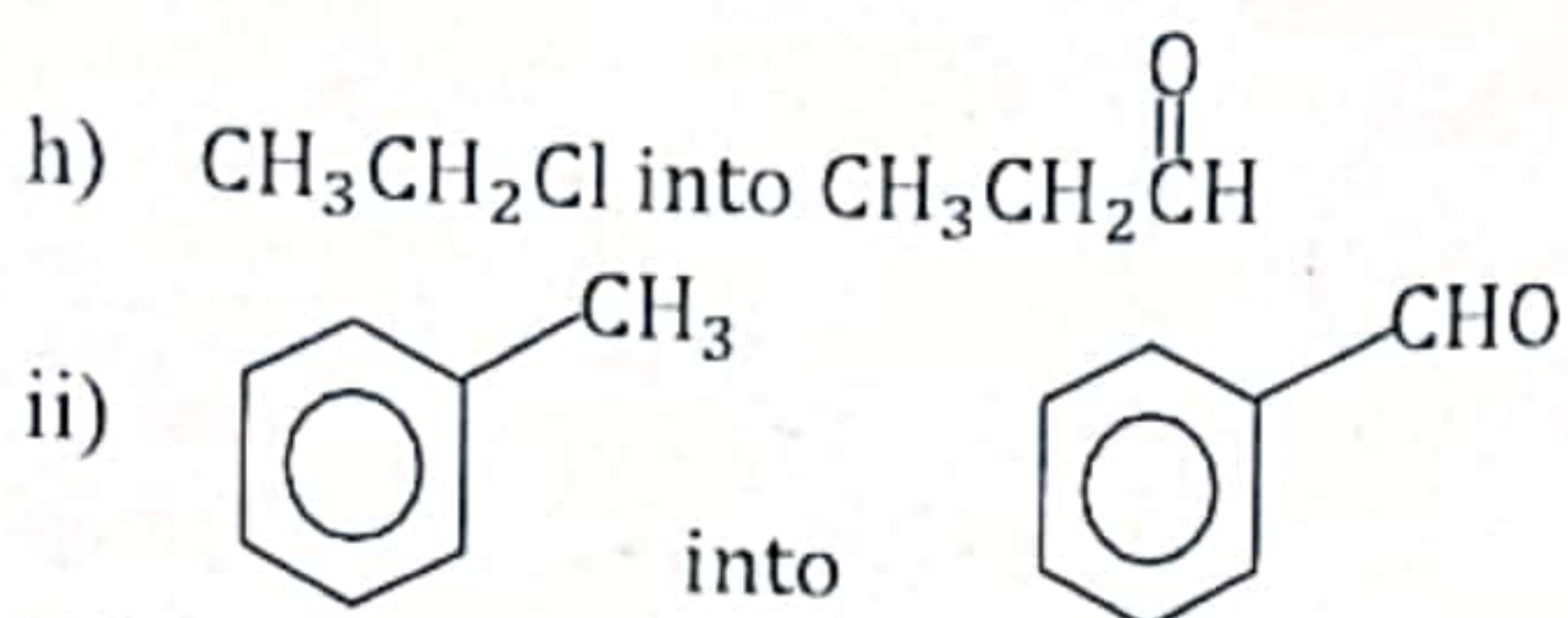
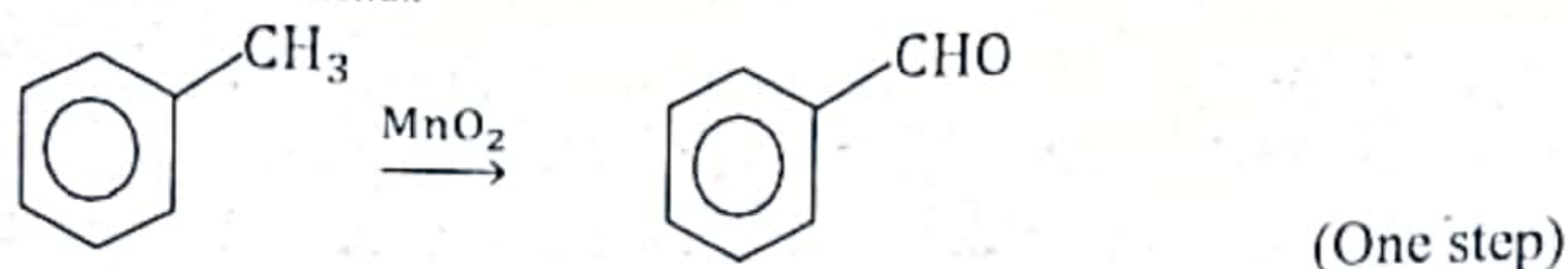
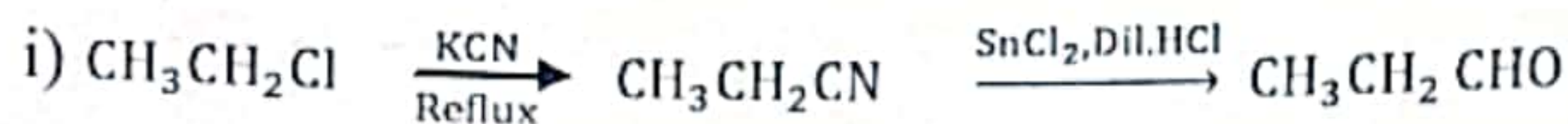
- In the above reaction, the use of BaSO_4 (sulphur containing compound) is to poison palladium catalyst so as to prevent further reduction of aldehyde to alcohol.

i.e

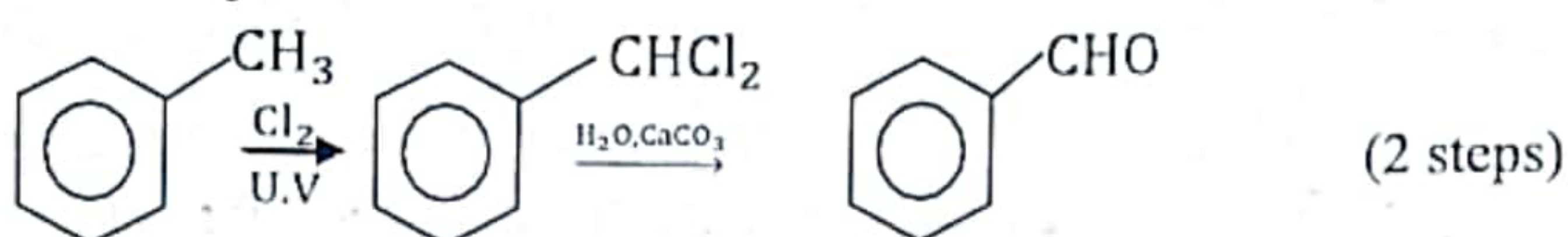


Example 3

Show how would you convert:

**Solution**

Alternatively;

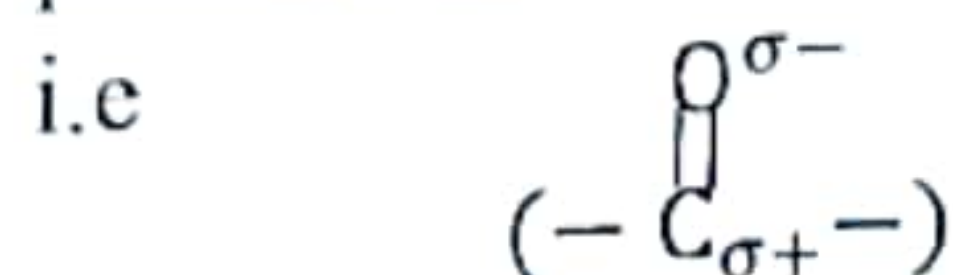
**PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS**

- In comparison to alcohols and carboxylic acids, carbonyl compounds has lower boiling point due to limited hydrogen bonding present in them.
- Among carbonyl compounds themselves, boiling point increases with an increase in number of carbon atoms in the compound.
- Carbonyl compounds are slightly soluble in water due to polarity of $\text{C}=\text{O}$ bond but are more soluble in organic solvents.

CHEMICAL REACTIONS OF CARBONYL COMPOUNDS**Nucleophilic addition reactions**

This is the characteristic chemical reaction of carbonyl compound.

- In carbonyl group ($-\text{C}(=\text{O})-$), oxygen being more electronegative than carbon, is negatively polarised and carbon is positively polarised



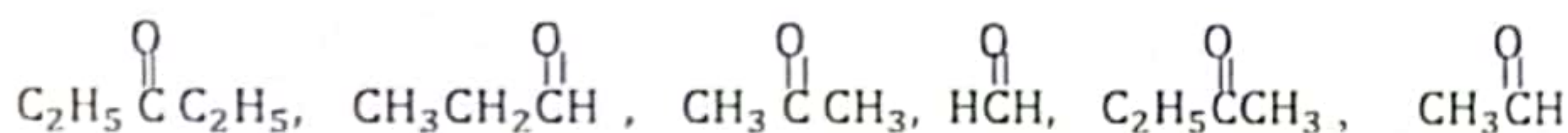
Thus carbon in carbonyl group is electrophilic and hence it becomes a good site for incoming nucleophile, yet there is π (double) bond in carbon of carbonyl group (functional group) then carbonyl compounds are more likely to undergo addition reaction and hence nucleophilic addition reactions.

- Ability of carbonyl compounds to undergo nucleophilic addition reaction depends on the amount of partial positive charge present in the carbon.
- If the carbon is more positively polarised then the compounds will be more likely to undergo nucleophilic addition reaction and vice-versa.
- On another hand the amount of partial positive charge present in the carbon is determined by the strength of positive inductive effect exerted by alkyl groups present in carbonyl group.

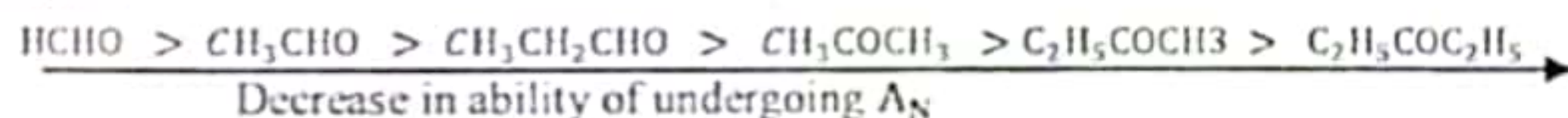
- If there is stronger positive inductive effect which is exerted then the carbon will be less positively polarised and vice versa.
- This explain why higher member of aldehyde are less reactive towards nucleophile than lower member (it because the strength of positive inductive effect increase with an increase in length of carbon chain of alkyl groups).
- The strength of positive inductive effect also explains why aldehydes are more reactive than ketones. This is because while in aldehyde, positive inductive effect is exerted by one alkyl group from one direction only, in ketone positive inductive effect is exerted by two alkyl groups from two directions, thus carbonyl group in ketone experience stronger positive inductive effect than in aldehyde.
- Another reason of high reactivity of ketone compared to those of aldehydes is the fact that; carbonyl group in ketone experience larger steric hindrance from (two) alkyl groups.
- This can also used to explain why carbonyl compound with larger alkyl group is less reactive towards nucleophile (in nucleophilic addition reaction) because steric hindrance increases with an increase in size of alkyl groups.

Example 4

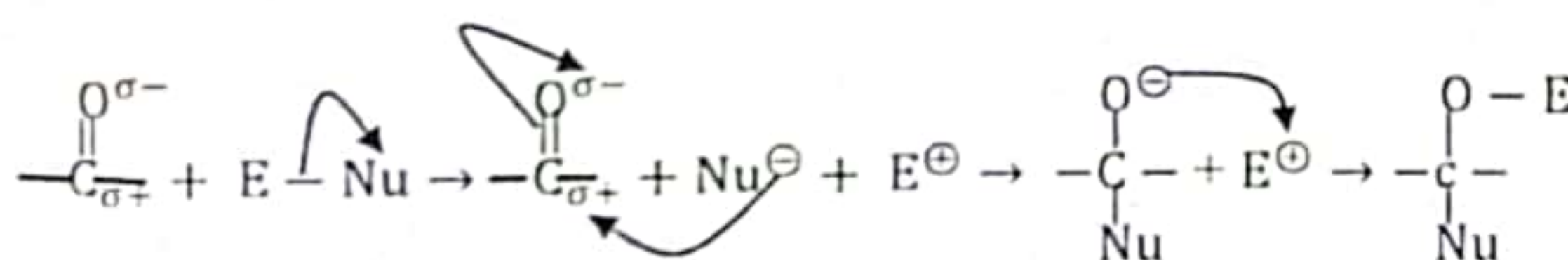
Arrange the following organic compounds according to ability of undergoing nucleophilic addition reactions



Solution

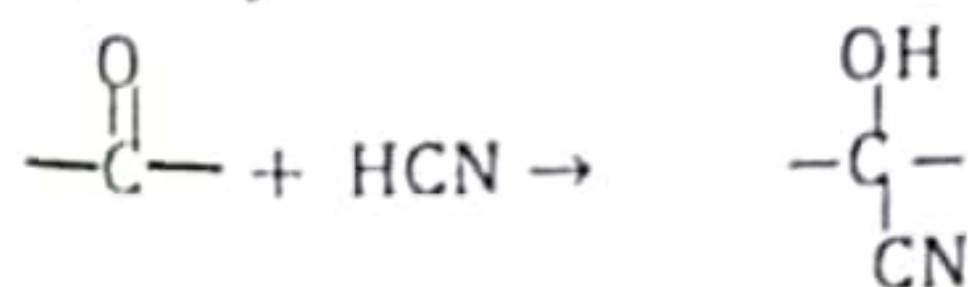


Generally carbonyl compound follow the following mechanism in nucleophilic addition reaction.

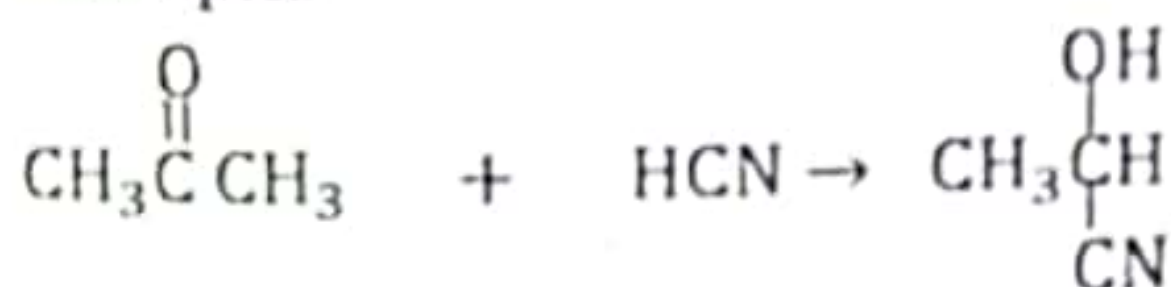
**Examples of nucleophilic addition reactions****i) Reaction with hydrogen cyanide (HCN)**

Carbonyl compounds react with HCN yielding cyanohydrin

Generally



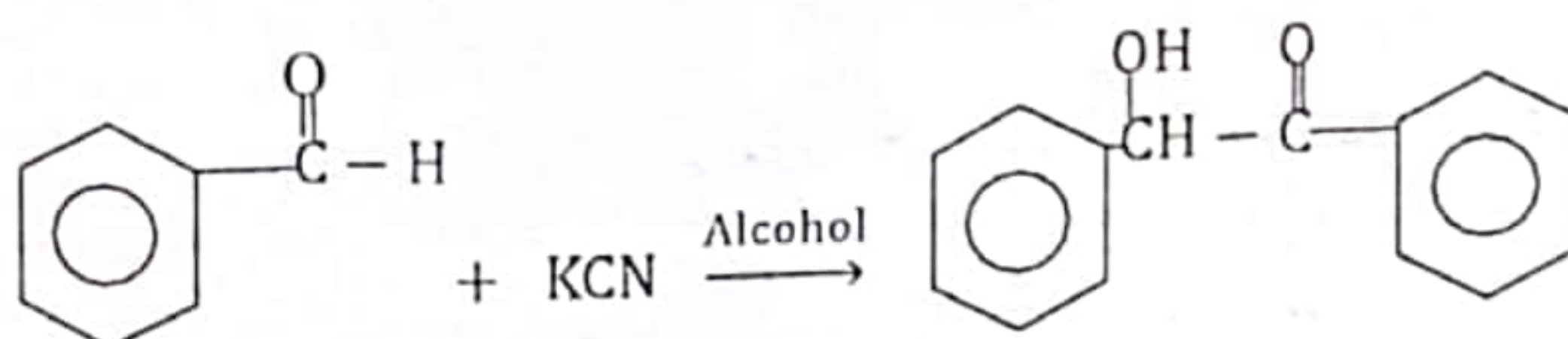
Examples



(HCN is commonly prepared by the reaction between NaCN and HCl as per equation

$\text{HCl} + \text{NaCN} \rightarrow \text{HCN} + \text{NaCl}$. So instead of HCN you may be given NaCN/HCl mixture to get the same result).

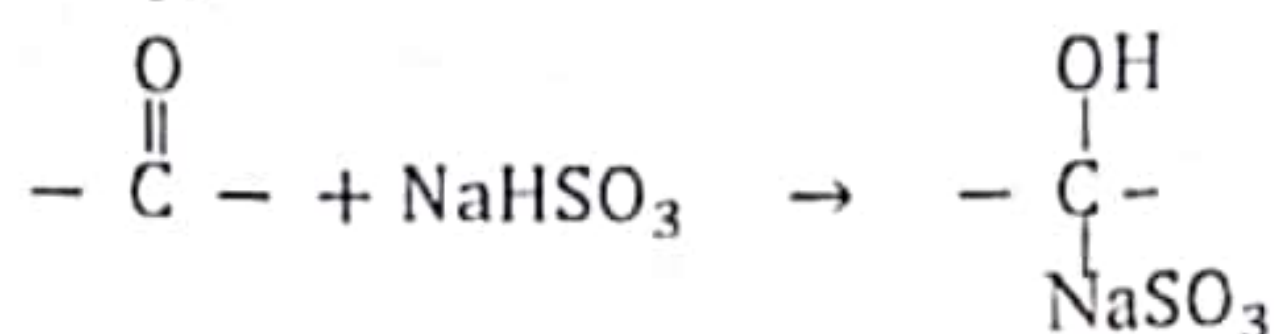
But



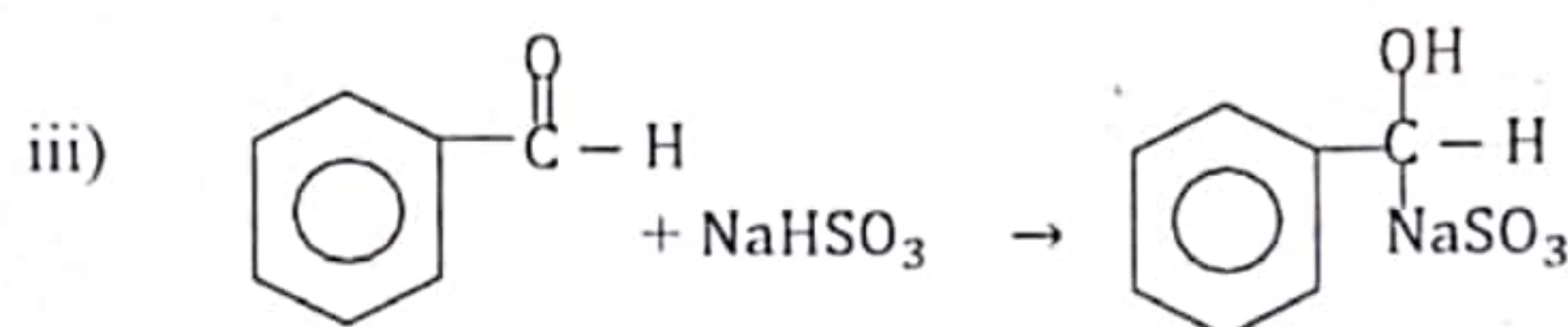
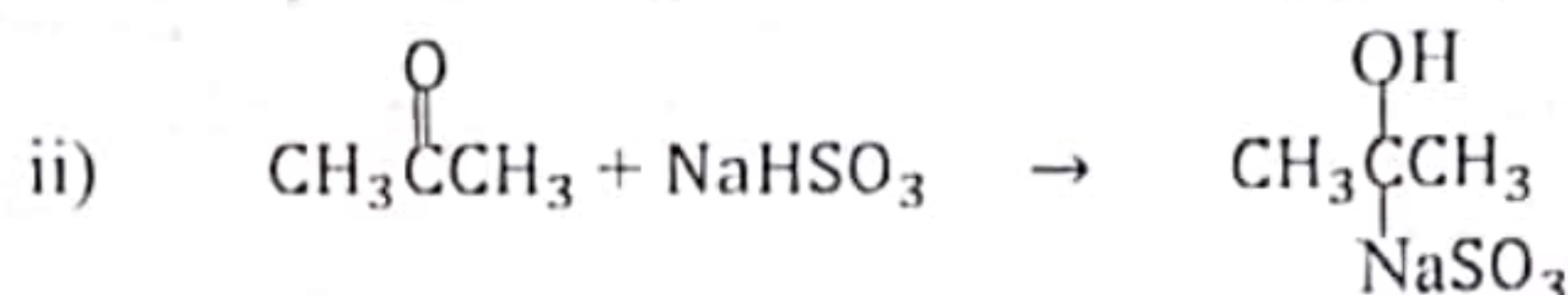
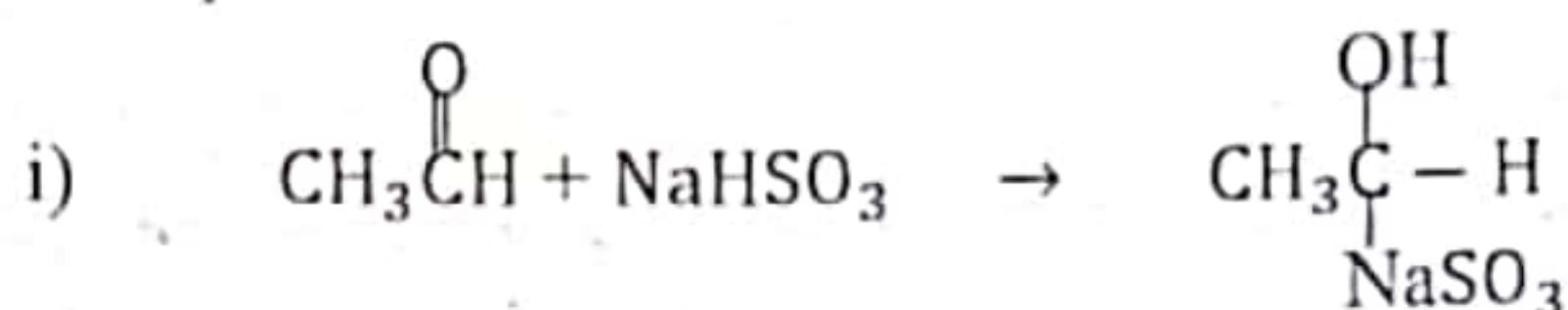
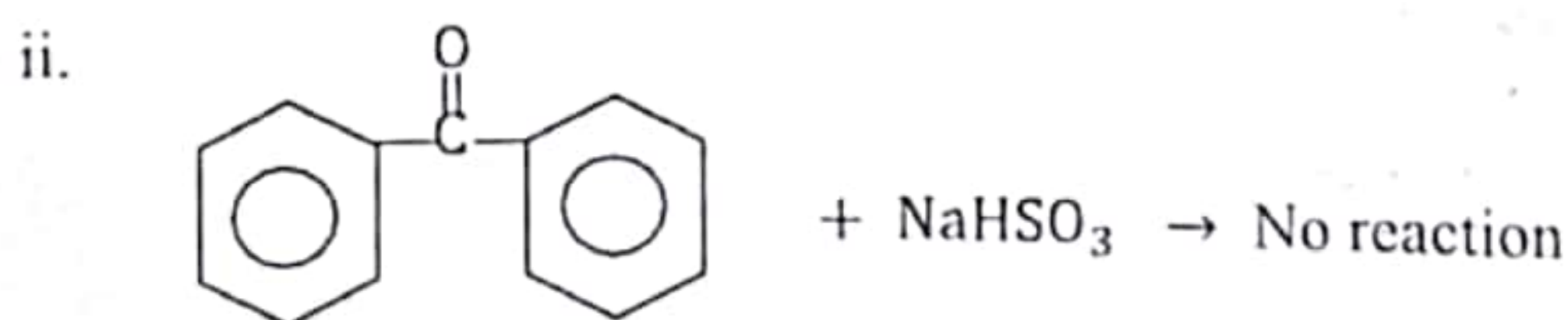
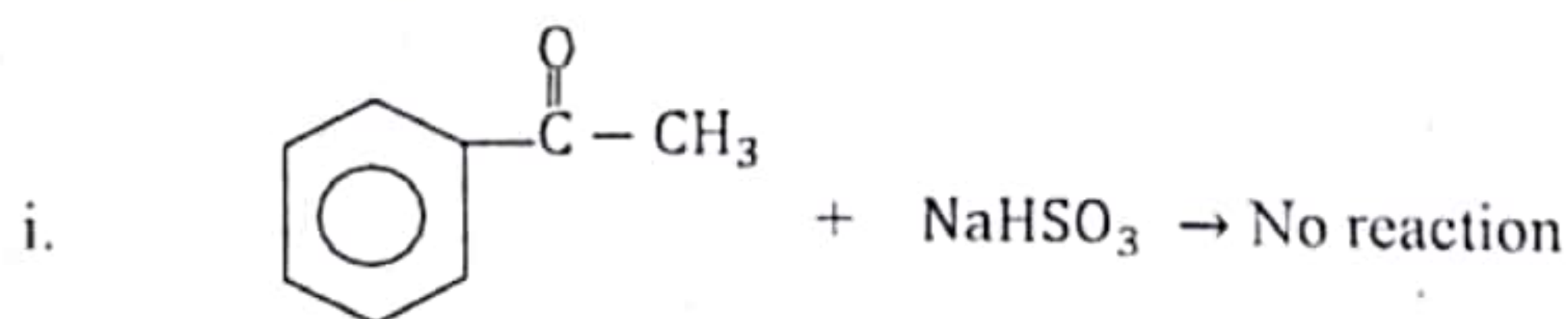
1, 2-diphenyl-2-hydroxyethanone

ii) Formation of bisulphiteCarbonyl compounds react with NaHSO_3 resulting to formation of bisulphite.

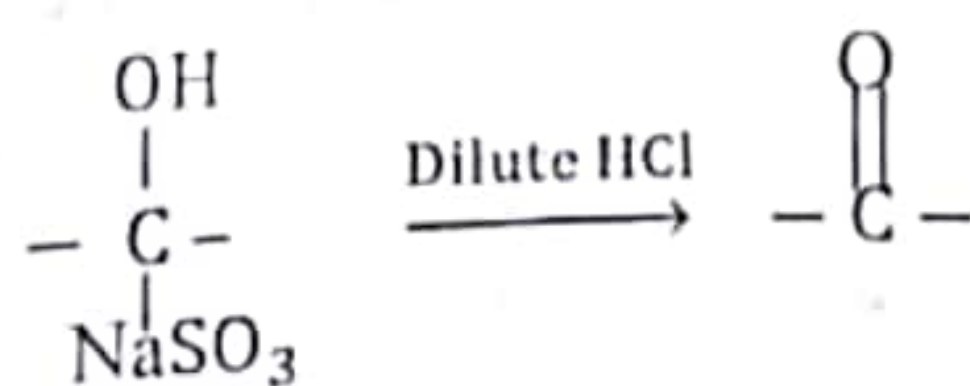
Generally;



Examples:

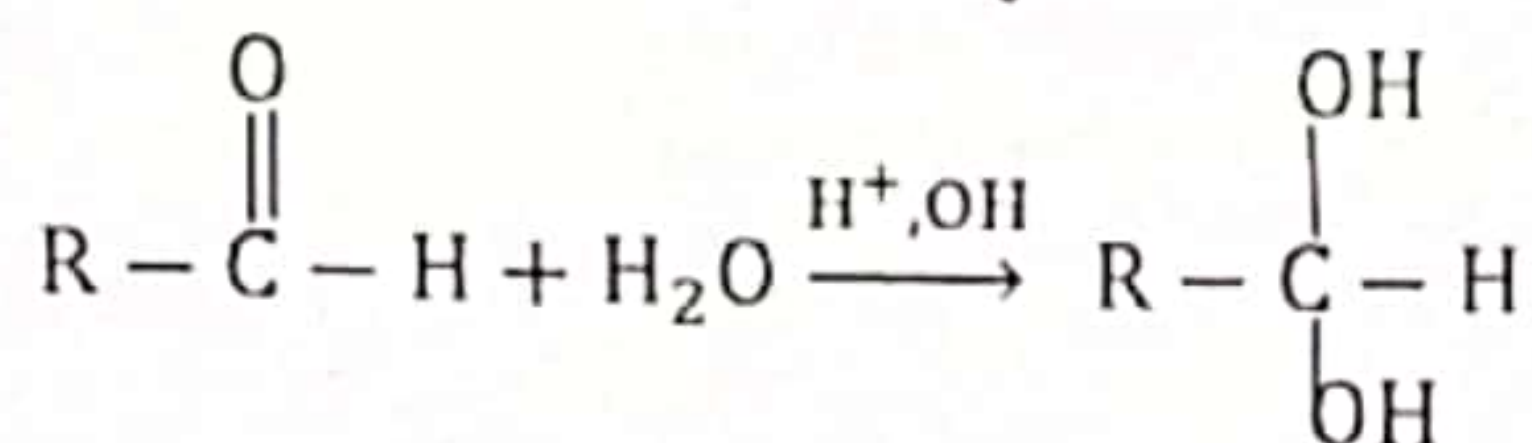
**Understand!**This reaction involves an addition of NaSO_3 which is very large molecule, so if there is large steric hindrance especially in aromatic ketone the reaction will not occur. For example;

The bisulphite is insoluble and can be regenerated to the original carbonyl compound by action of dilute acids and hence the reaction is very useful in separation (purification) of carbonyl compounds.

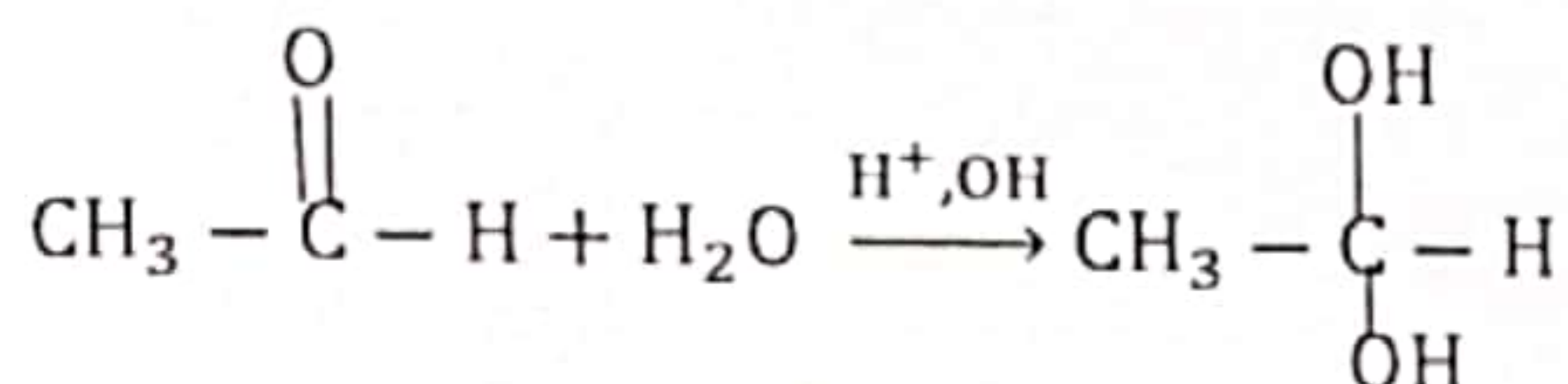


iii) Addition of water

The addition of water to aldehyde results to formation of hydrate



For example

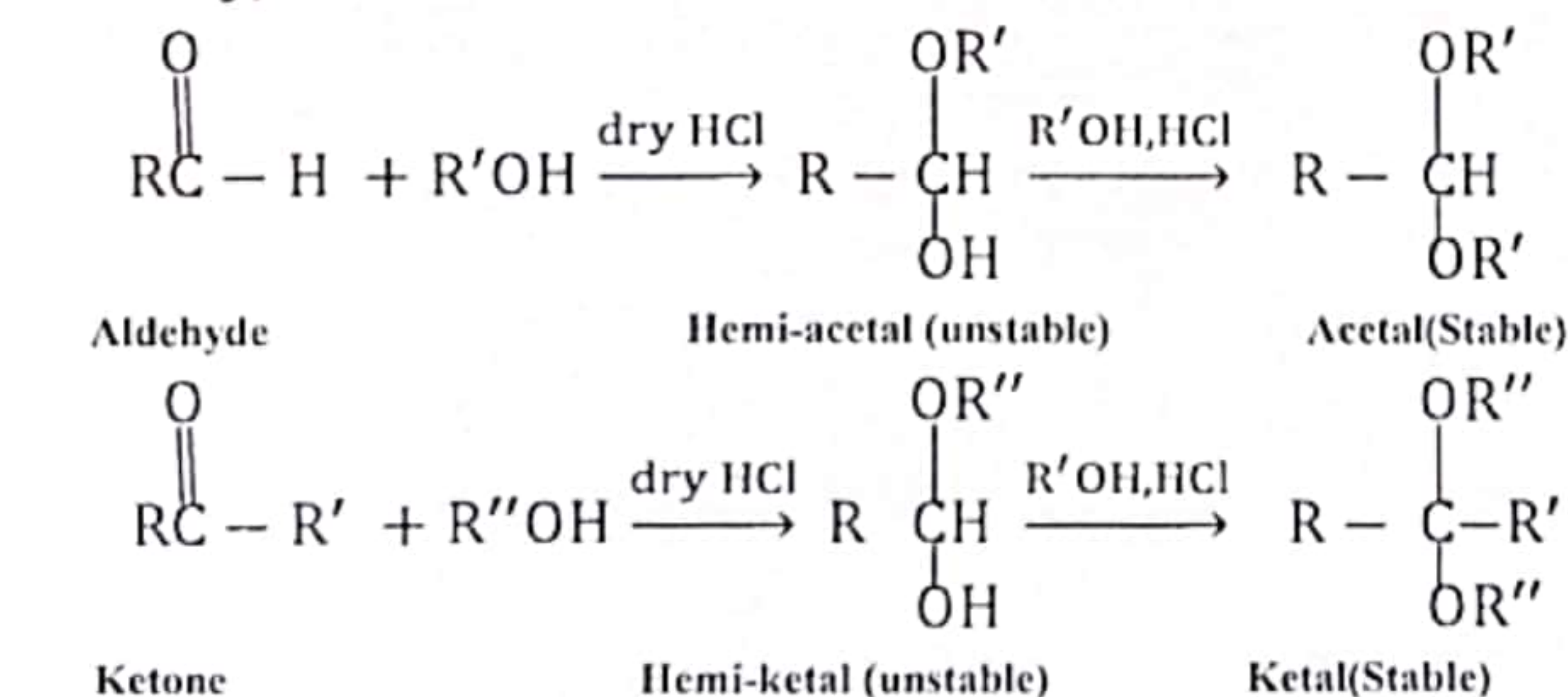


But ketone does not form stable hydrate.

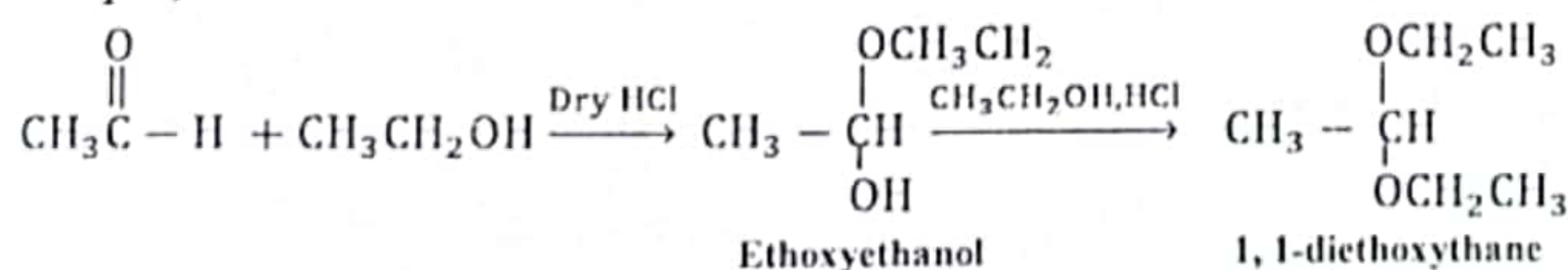
iv) Reaction with alcohols

Carbonyl compounds react with alcohol in presence of dry acid catalyst to form **hemi-acetal** (a family of organic compounds with functional group consisting of one -OH and one -OR group bonded to the same carbon) which is unstable but if alcohol present in excess a stable **acetal** (a family of organic compounds with functional group consisting of two -OR groups bonded to the same carbon) is formed.

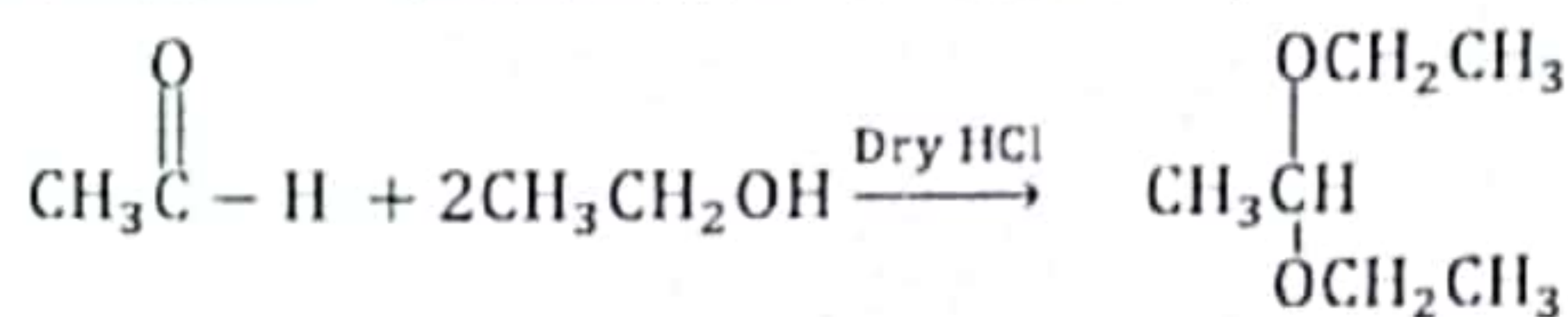
Generally;



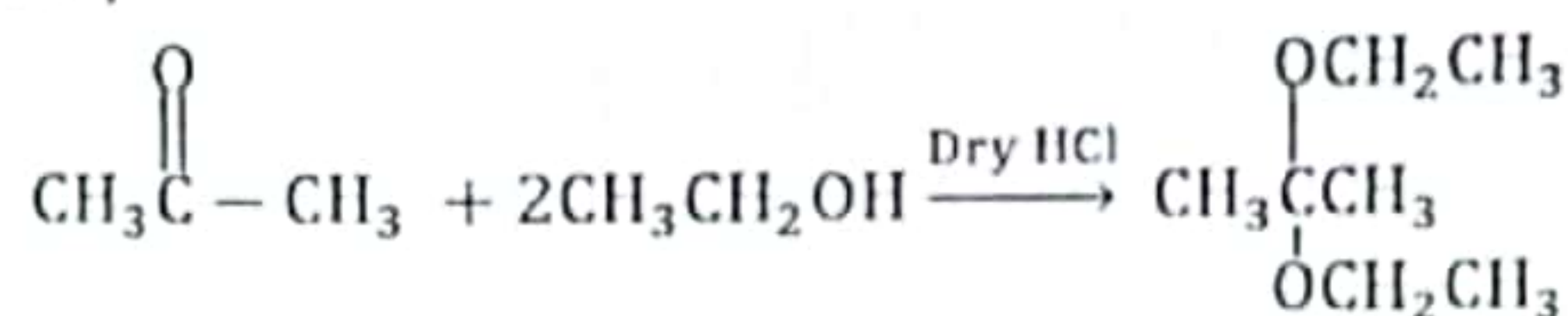
Example,



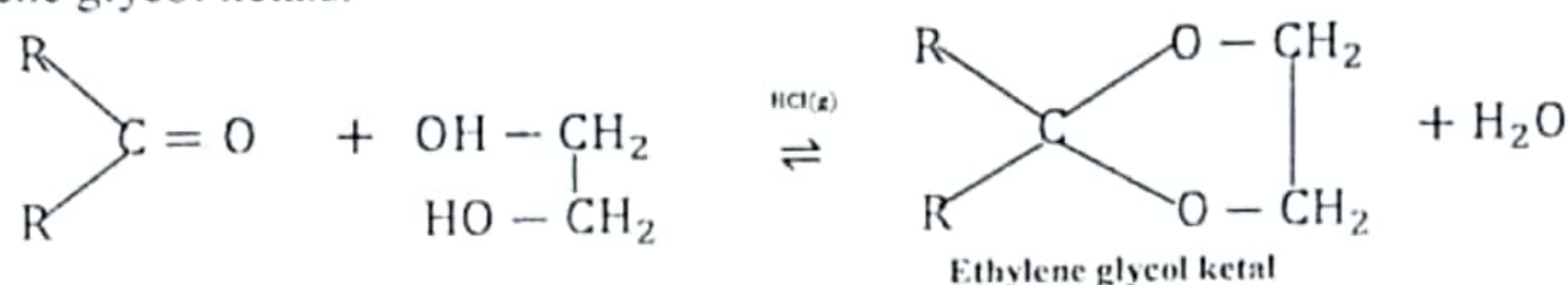
Thus overall reaction can be written as,



Also;



Similarly ketones react with 1,2 - ethanediol(ethylene glycol) to form cyclic product known as ethylene glycol ketals.

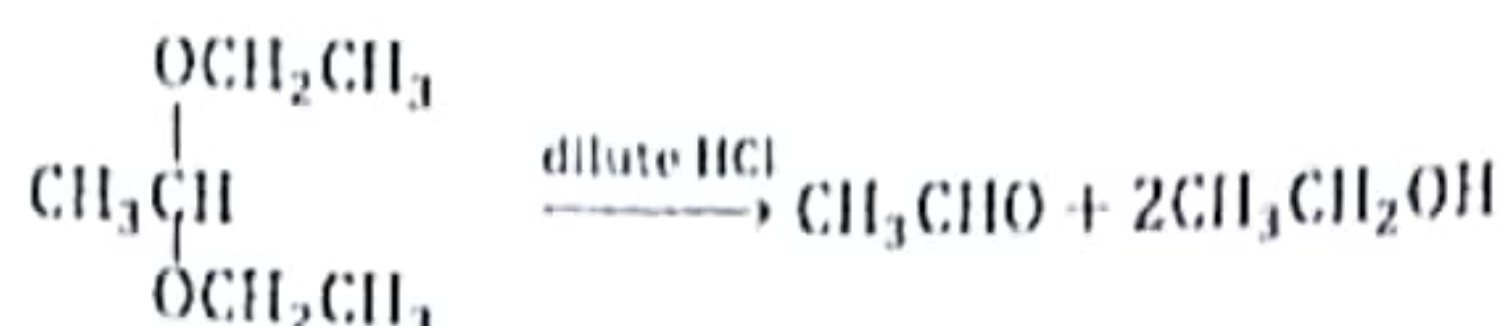


In the above reaction, why HCl must be dry?

This is simply because dry HCl absorbs the water produced in the reaction, thus shifting position of equilibrium to the right and therefore favouring formation of acetals and ketals.

– On another hand dilute HCl hydrolyse acetal and ketal favouring backward reaction.

For example;



Very important!

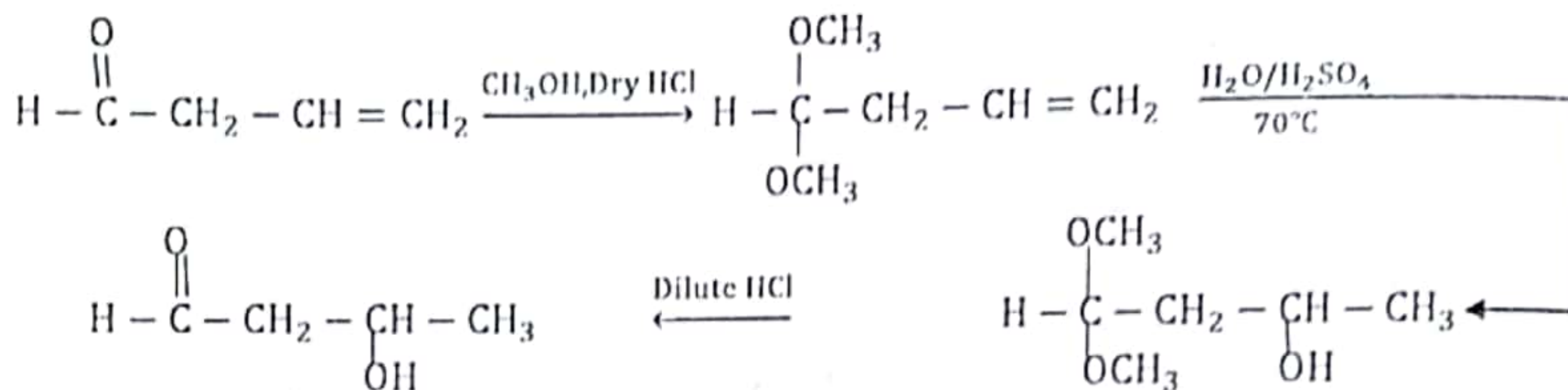
To understand that, ability of aldehyde to be regenerated from acetal under acidic solution makes an acetal good **protecting group**.

- A **protecting group** is a group that is introduced into a molecule to prevent the reaction of sensitive group while a reaction is carried out at some other site in the molecule.
- The protecting group must have the ability to react back to regenerate the original group from which it was formed.

Example 5

Show how would you convert $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}=\text{CH}_2$ into $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$

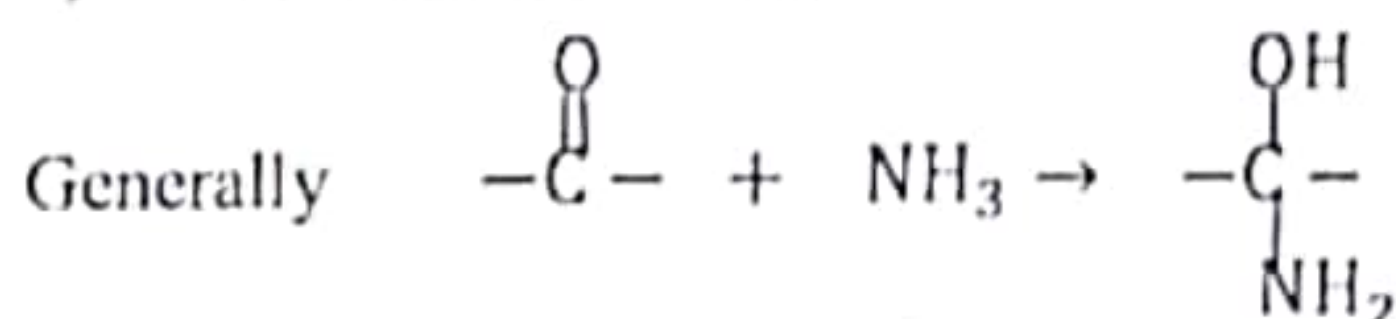
Solution



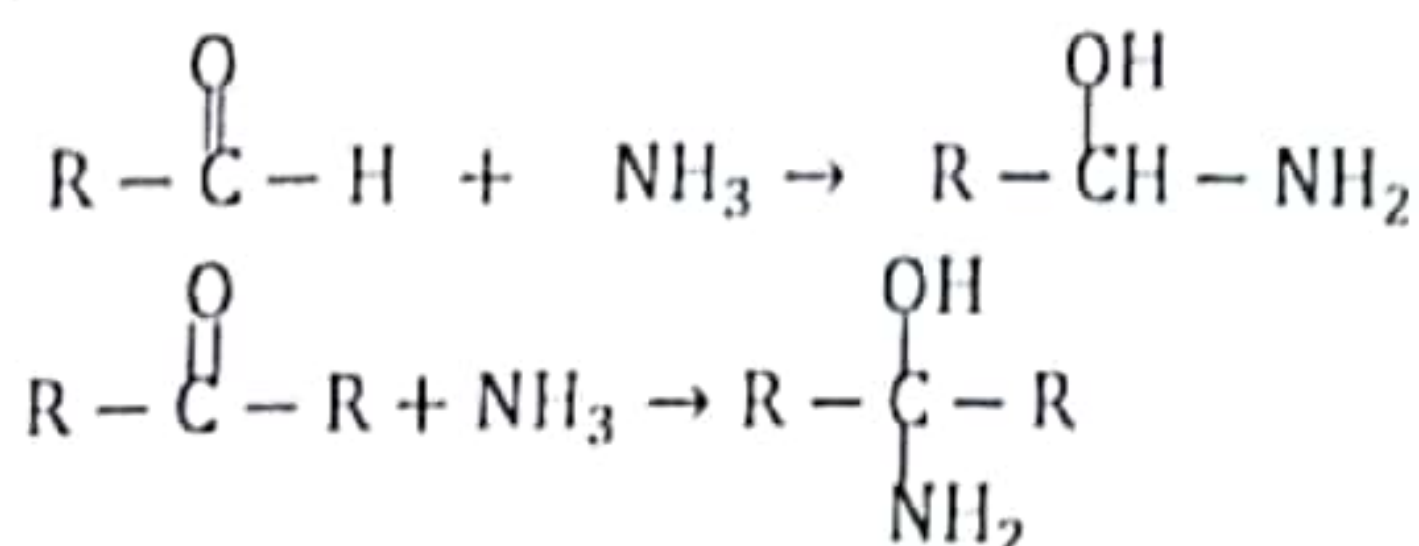
Things to note from above conversion:

- In the first step acetal is formed to prevent aldehyde group to react with water keeping in mind that aldehyde group react with water under presence of acid (H_2SO_4) to give hydrate.
- In the second step the reaction takes place at $\text{C}=\text{C}$ only because the aldehyde group has been protected through acetal formation in the first step.
- In the last step, the aldehyde group is easily regenerated by action of dilute acid on the acetals.

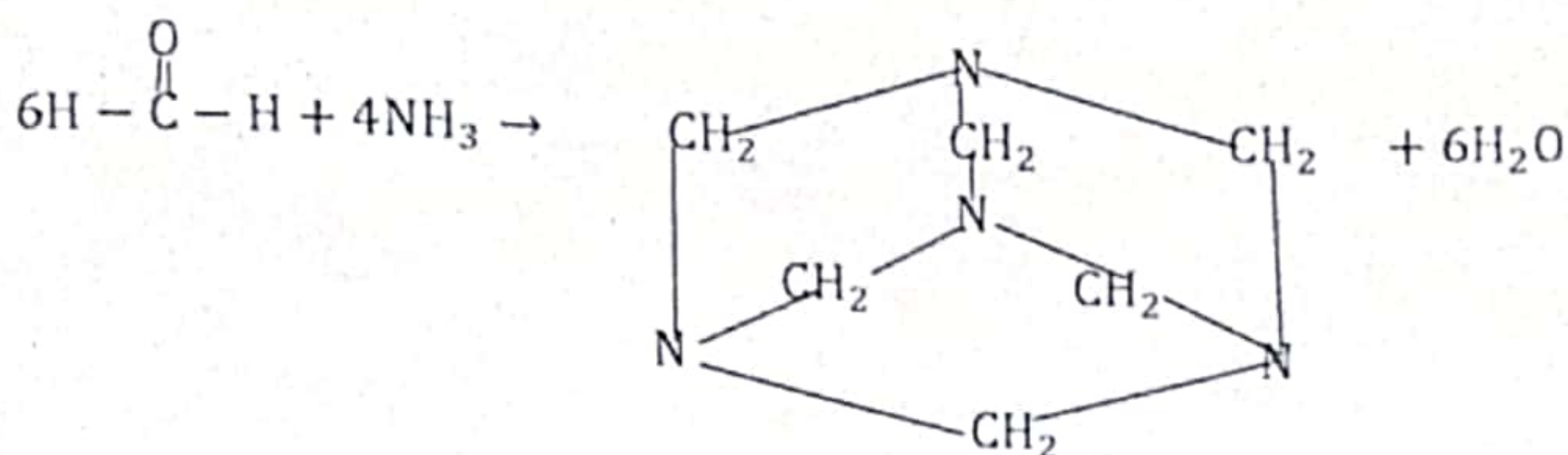
v) Addition of ammonia



For example,



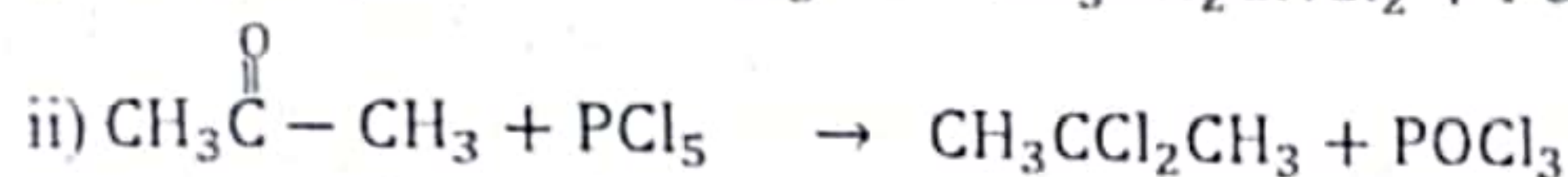
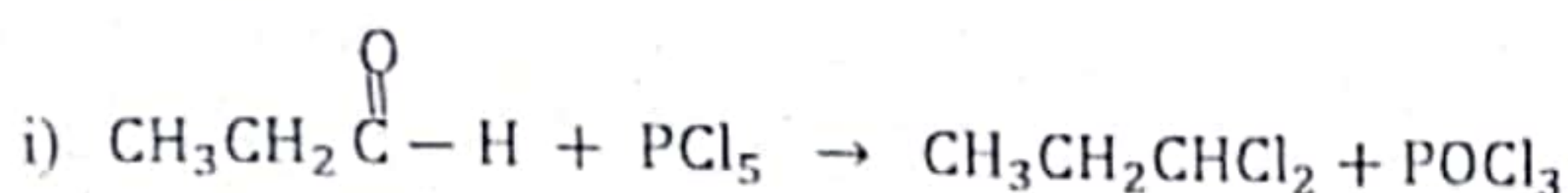
But;



Nucleophilic substitution reaction

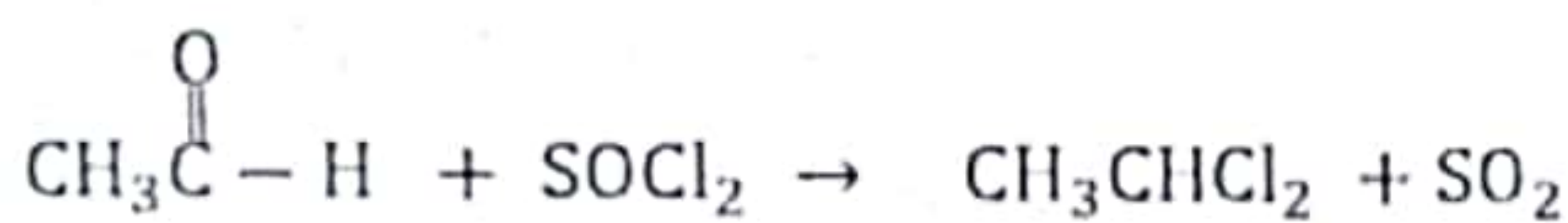
When carbonyl compound is treated with halogenating agent like PCl_5 , oxygen in carbonyl group is replaced by halogens.

Examples:

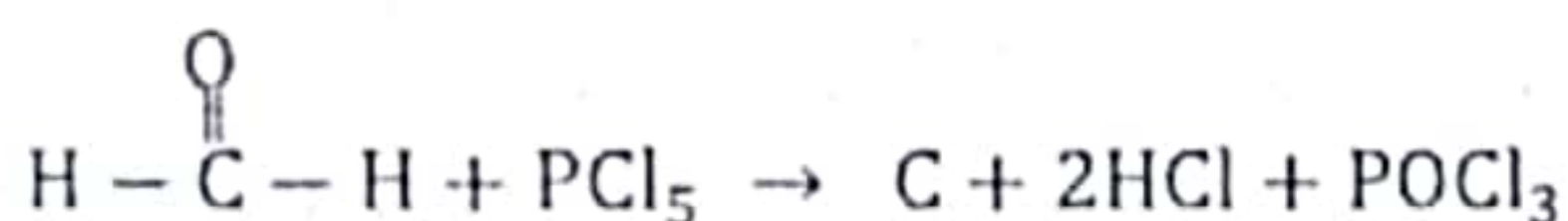


In above examples the reaction is similar to that in alcohol the only difference is that HCl is not involved (like in alcohol, since there is no OH group)

Similarly



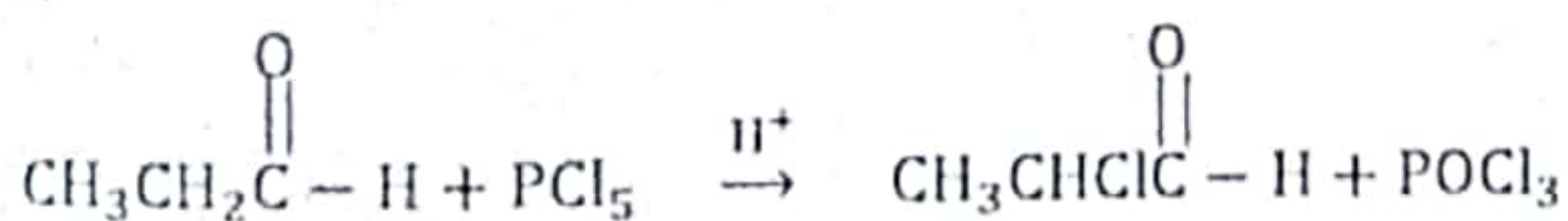
But



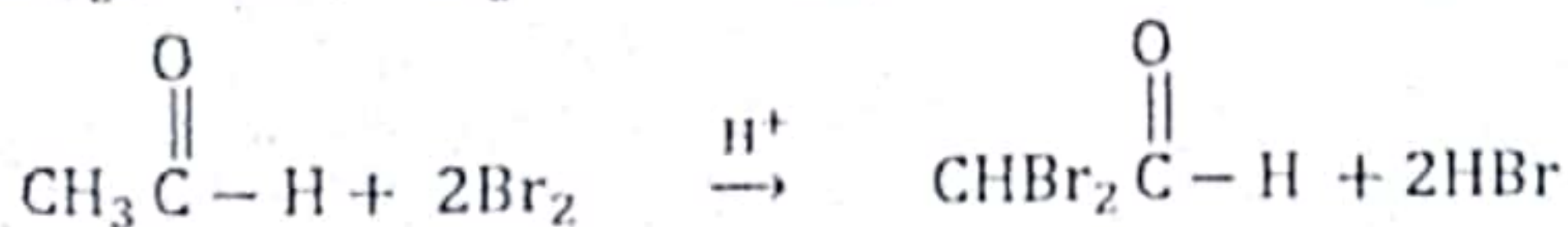
You should know that:

Carbonyl compound with alkyl group directly bonded to carbonyl group can react with halogens in presence of acidic medium in different way (without interference of carbonyl group). For example;

i)

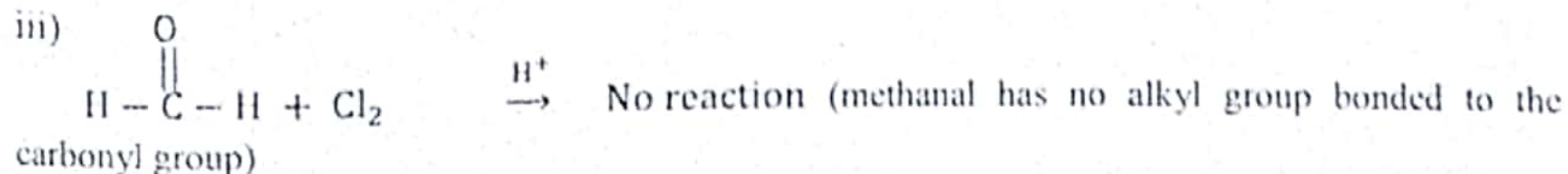


ii)

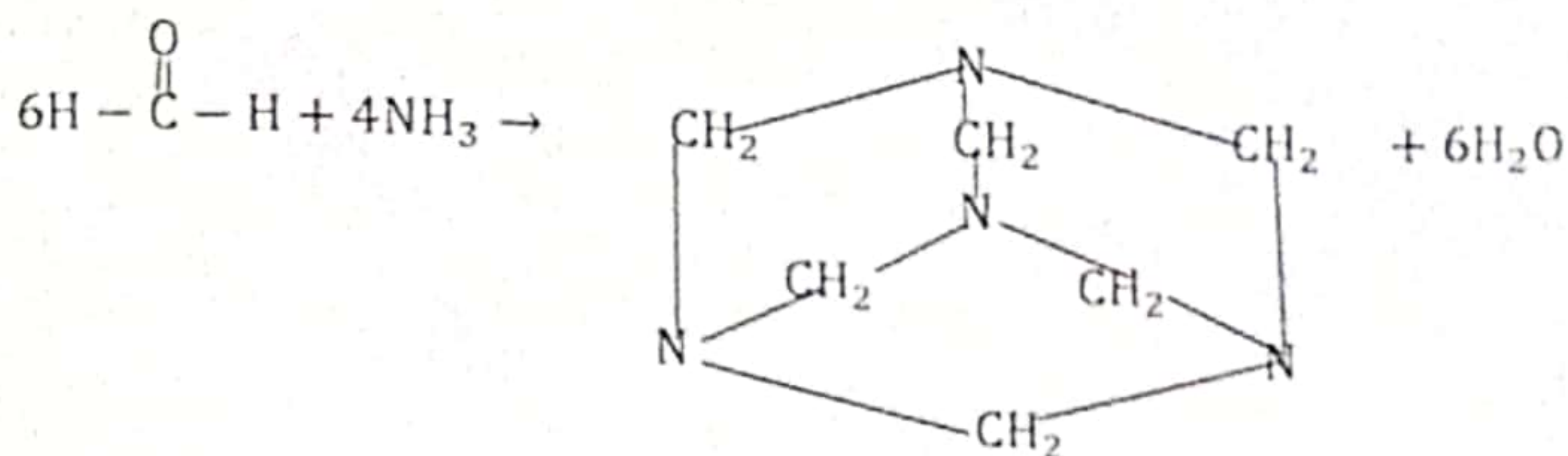


But;

iii)



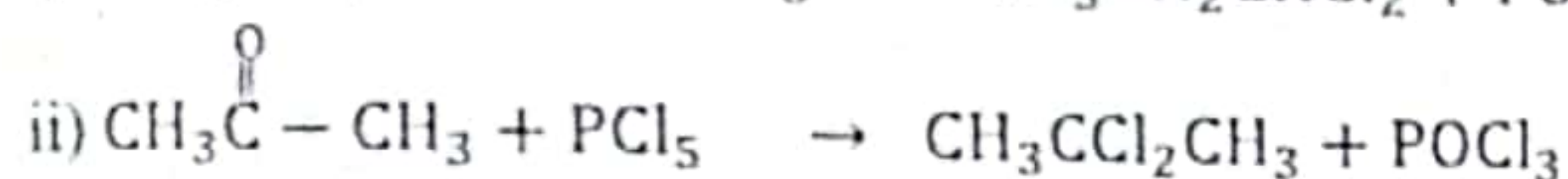
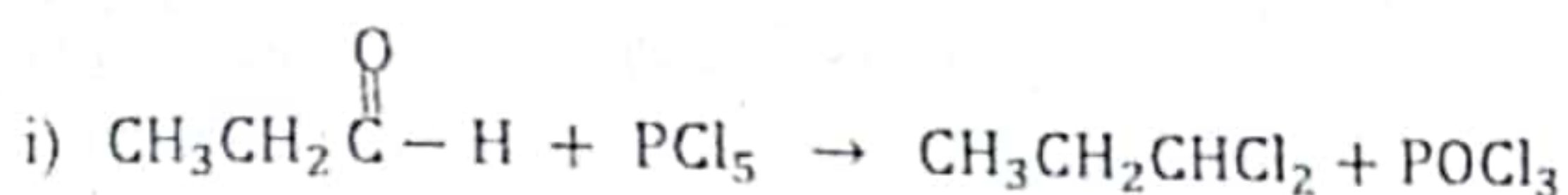
But;



Nucleophilic substitution reaction

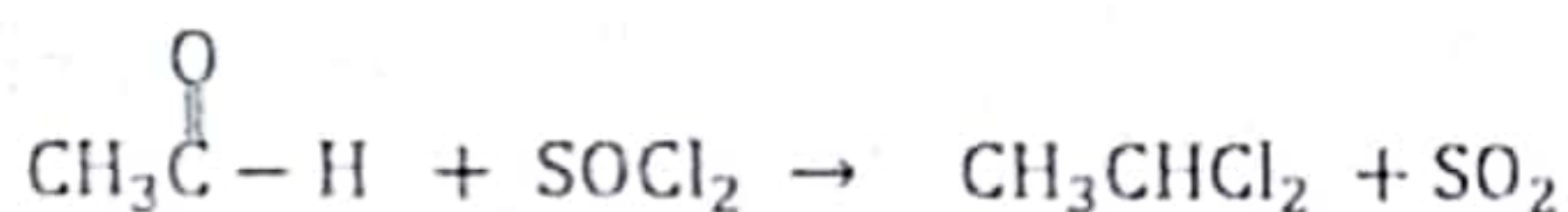
When carbonyl compound is treated with halogenating agent like PCl_5 , oxygen in carbonyl group is replaced by halogens.

Examples:

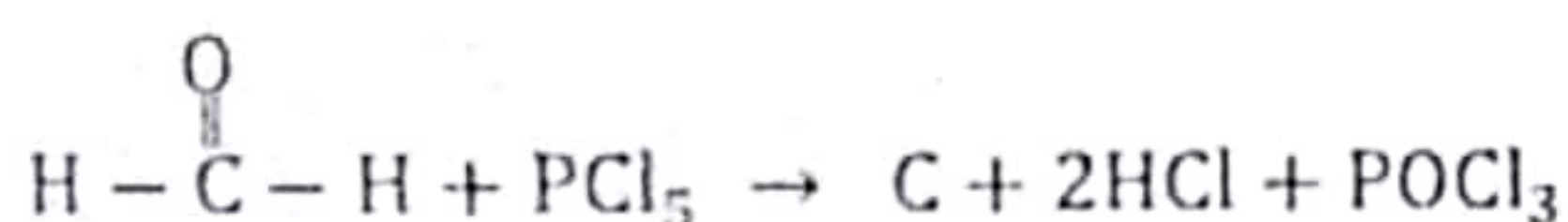


In above examples the reaction is similar to that in alcohol the only difference is that HCl is not involved (like in alcohol, since there is no OH group)

Similarly



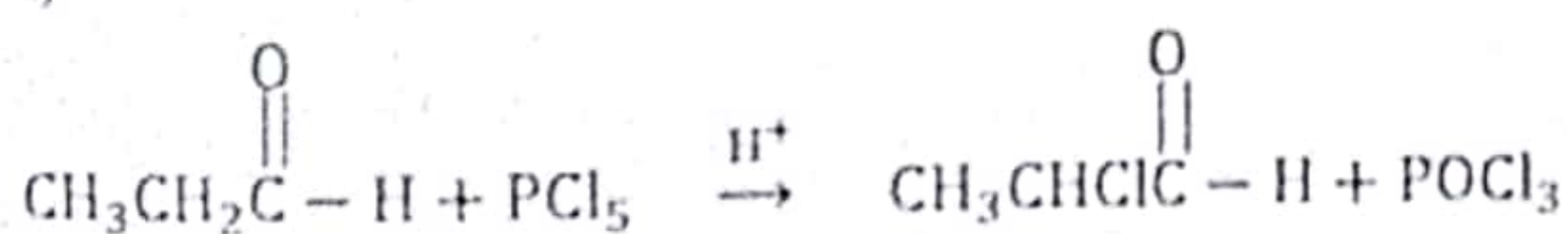
But



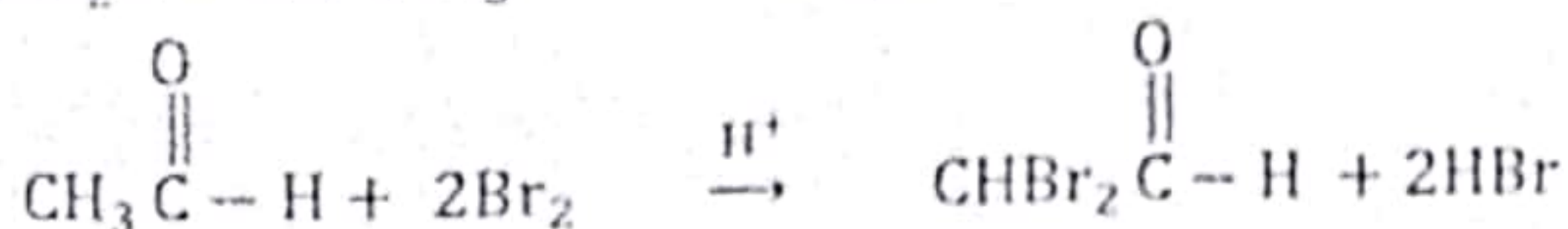
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Carbonyl compound with alkyl group directly bonded to carbonyl group can react with halogens in presence of acidic medium in different way (without interference of carbonyl group). For example;

i)

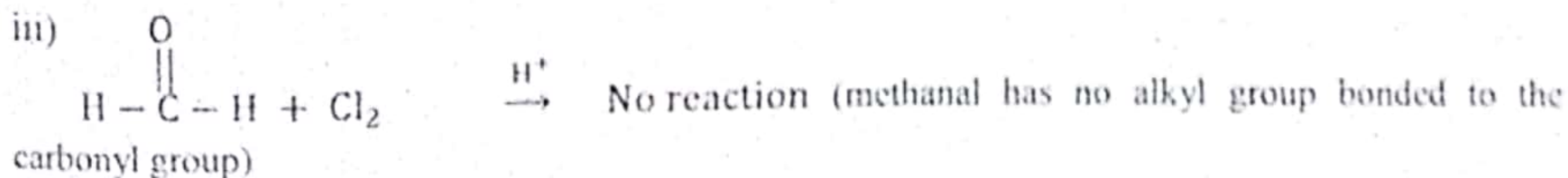


ii)



But;

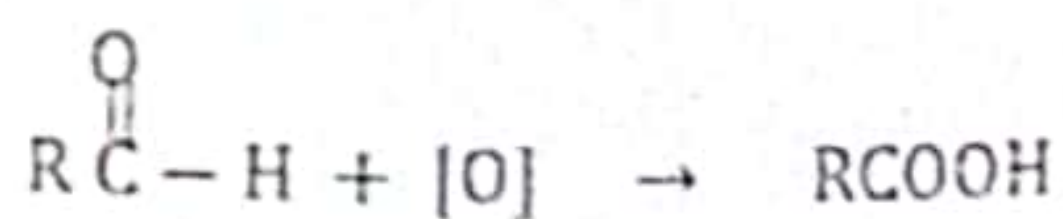
iii)



Oxidation

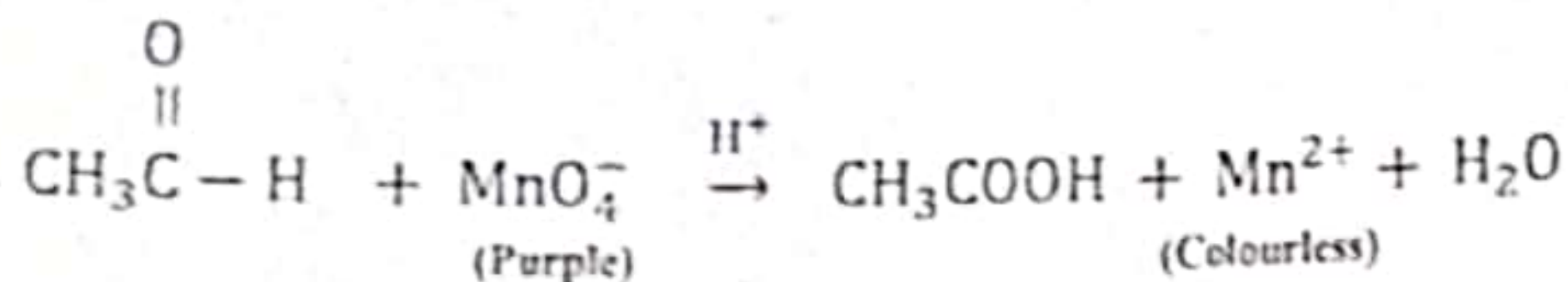
Aldehydes are good reducing agents, i.e they can be easily oxidised to carboxylic acids.

Generally;

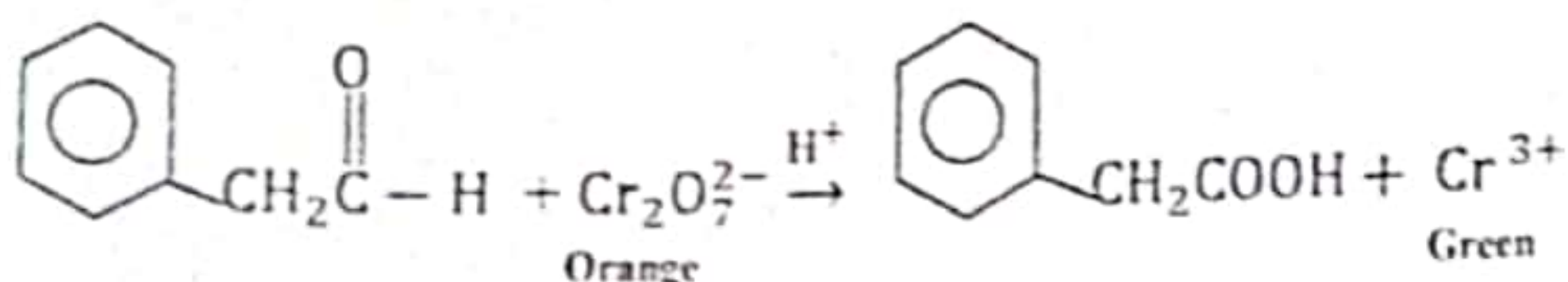


Examples:

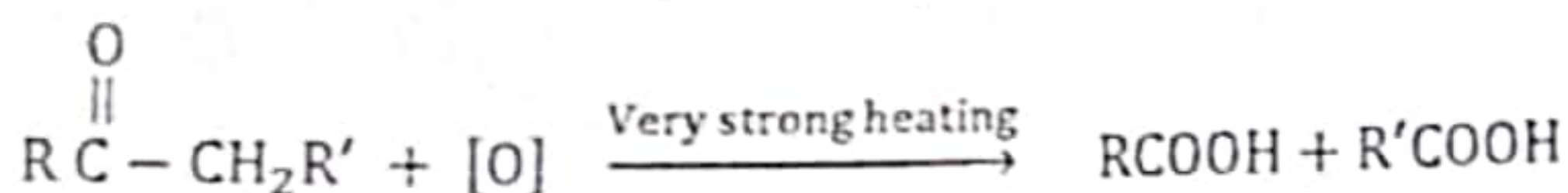
i)



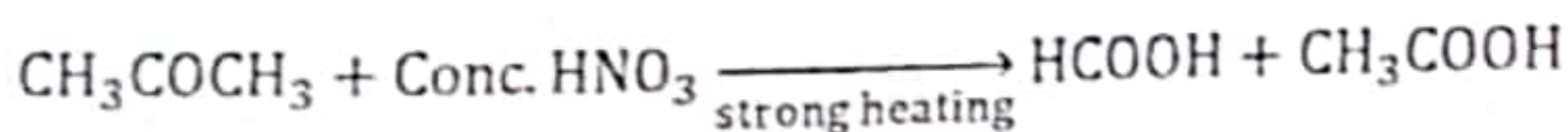
ii)



Ketones resist oxidation but they can undergo oxidation under very vigorous condition.



Similarly;

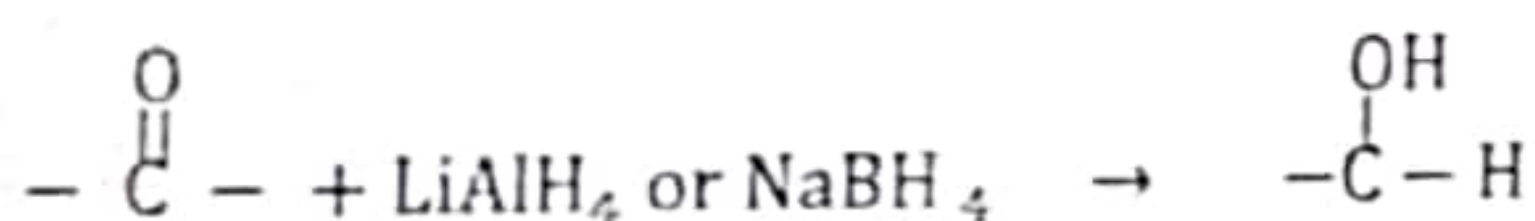


Reduction

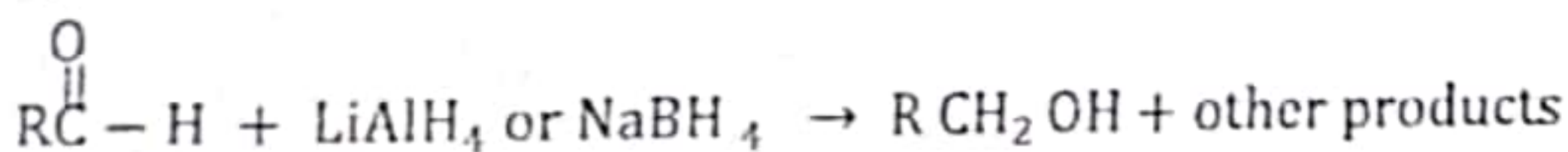
i. Formation of alcohol

Carbonyl compound reacts with reducing agent like LiAlH_4 and NaBH_4 to form alcohol.

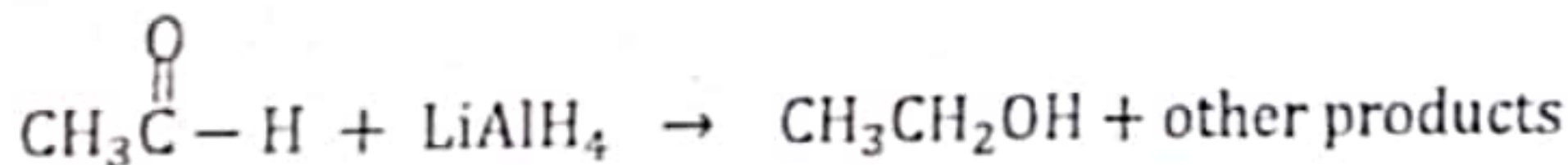
Generally,



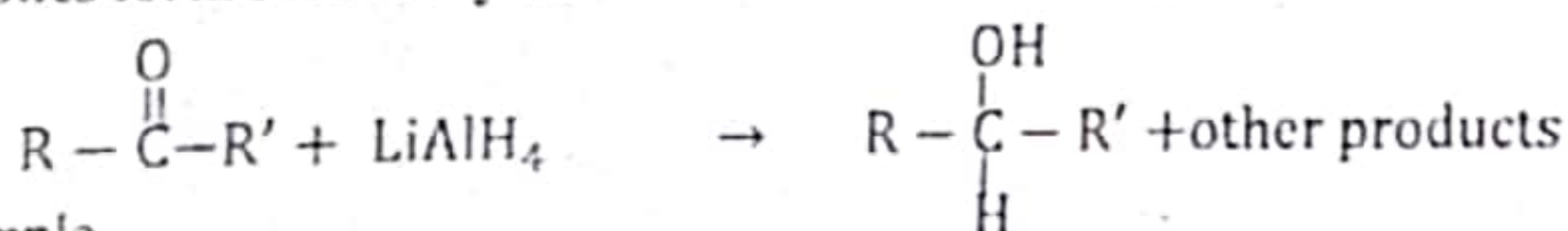
Aldehyde form primary alcohol.



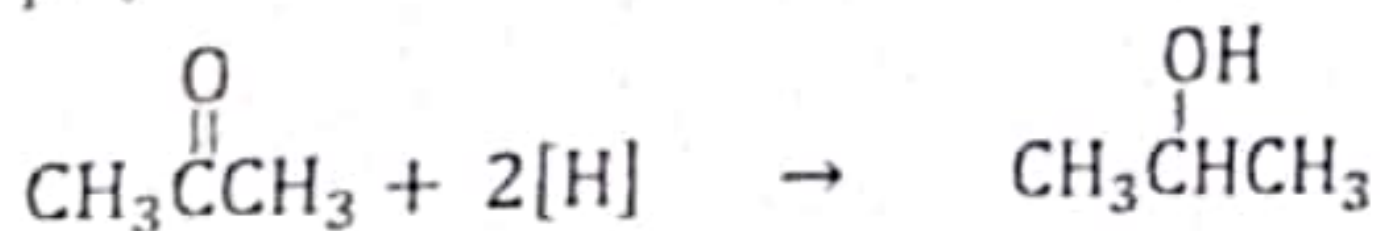
Example,



Ketones form secondary alcohol



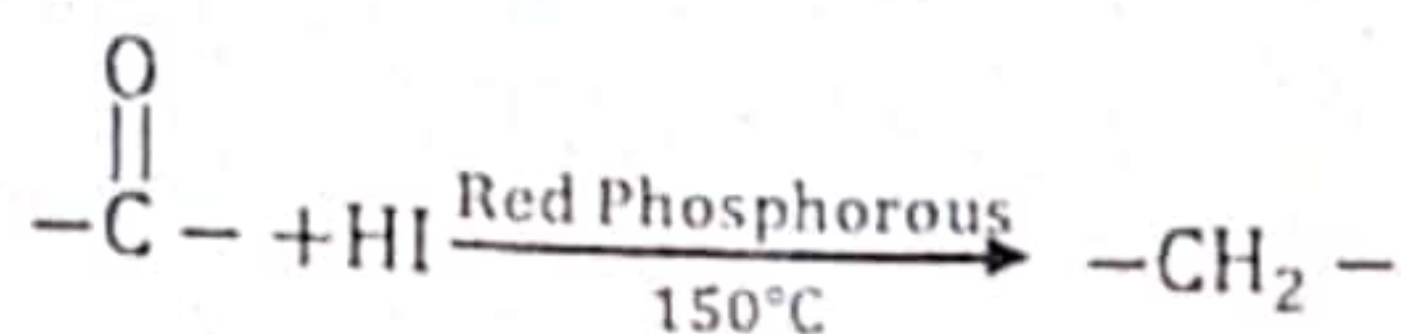
Example,



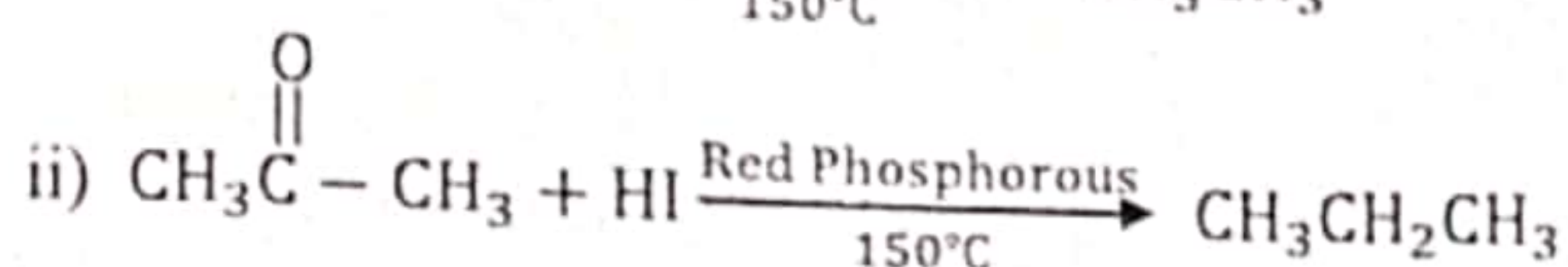
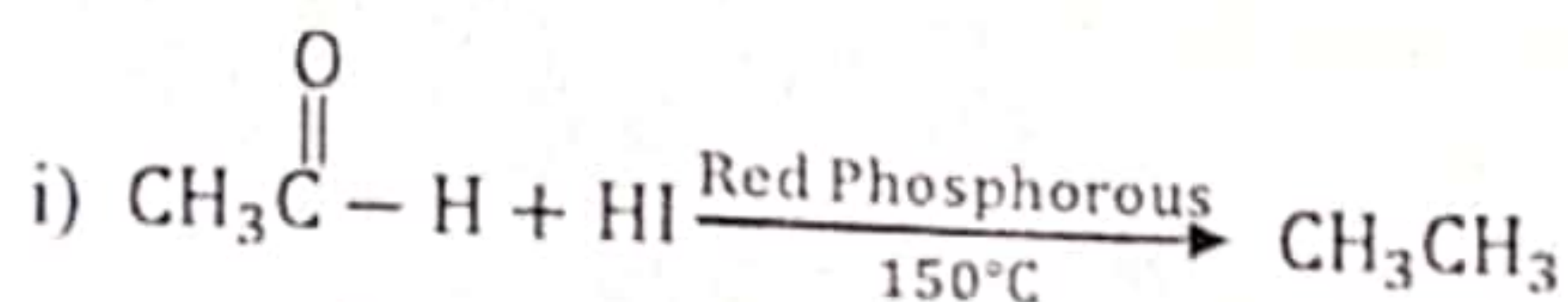
ii. Formation of alkane

Carbonyl compounds react with hydroiodic acid in presence of red phosphorous at temperature of 150°C to form alkane.

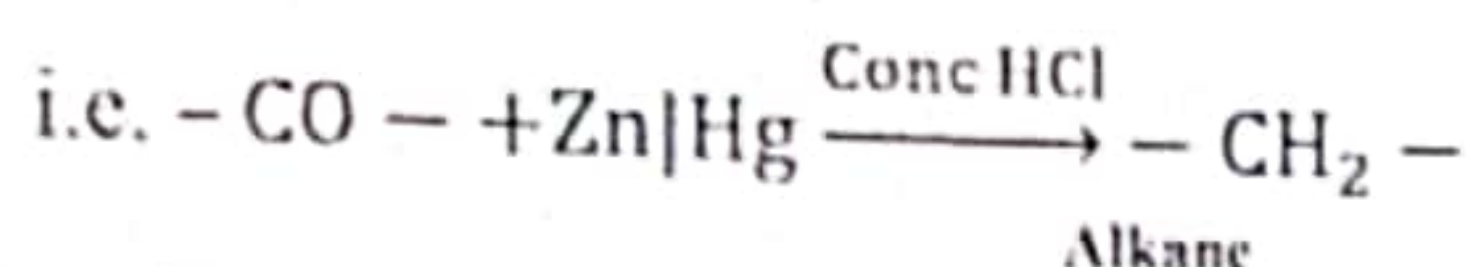
Generally;



Example,

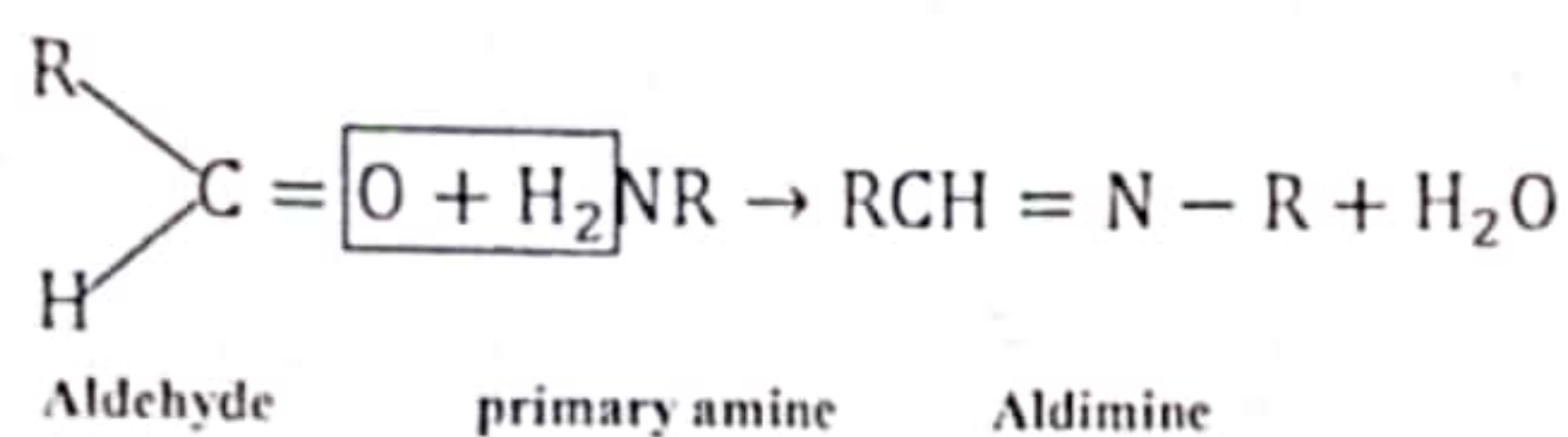


Alkanes can also be formed from a reaction between carbonyl compounds with a mixture of concentrated hydrochloric acid and amalgamated zinc (zinc amalgam) which is the mixture of zinc and mercury and the reaction is known as **Clemmensen's reaction**.

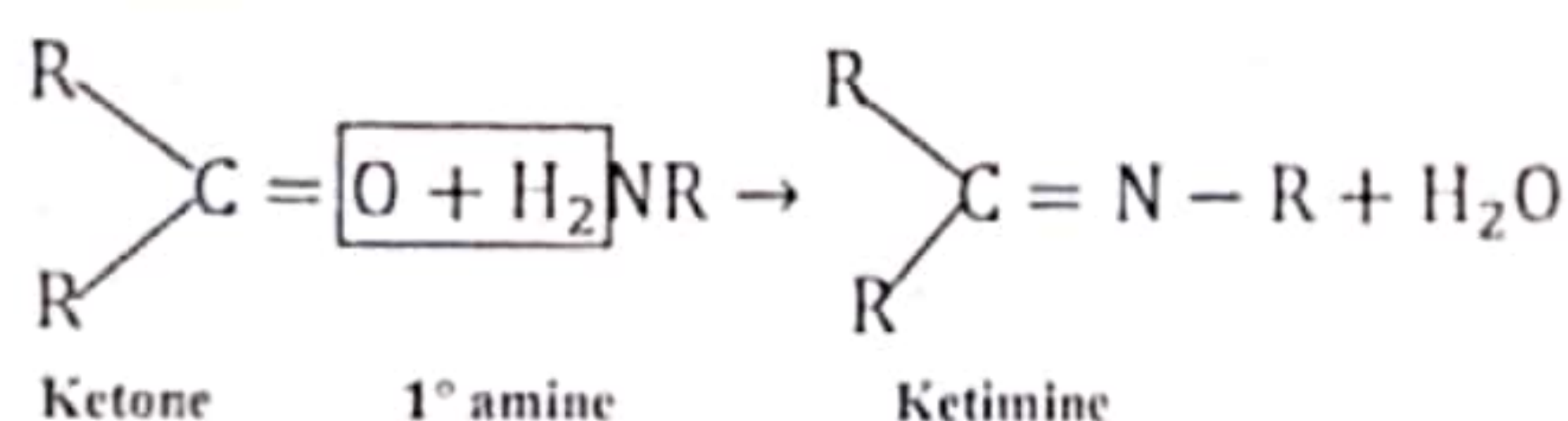


iii. Reaction with amine

Reaction of carbonyl compounds with amines gives **Schiff's bases** which are also known as **imines**. That is;



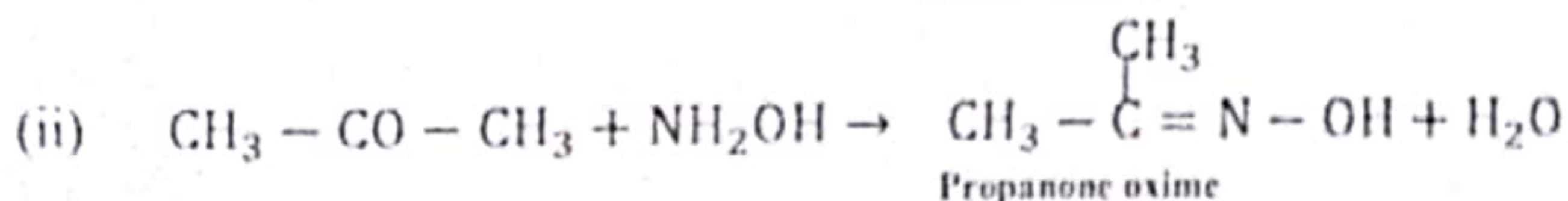
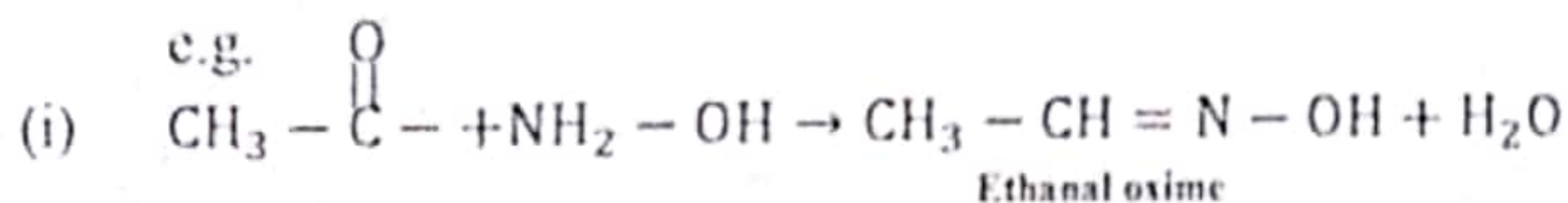
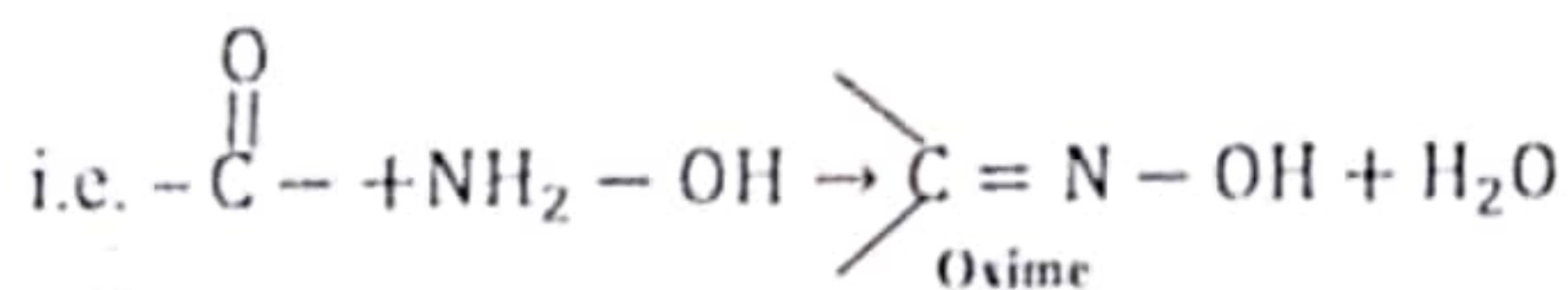
Or



For example: $\text{CH}_3\text{CHO} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{CH} = \text{NCH}_3 + \text{H}_2\text{O}$

iv. Reaction with hydroxylamine

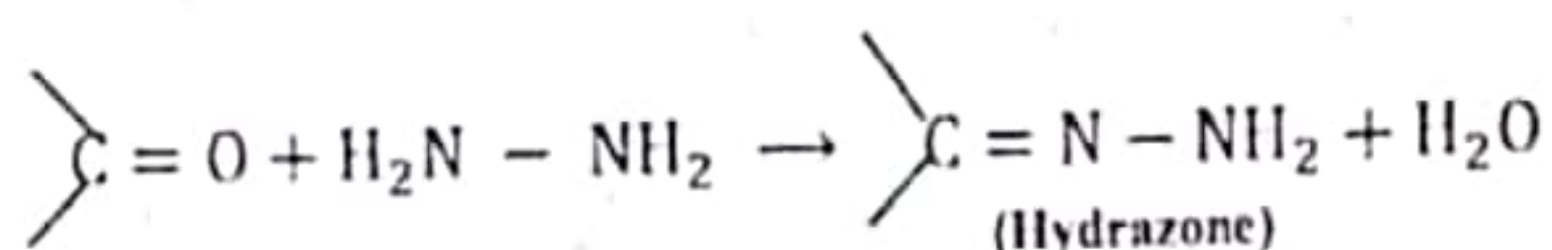
Carbonyl compounds reacts with hydroxylamine ($\text{NH}_2 - \text{OH}$) to give **oxime**.



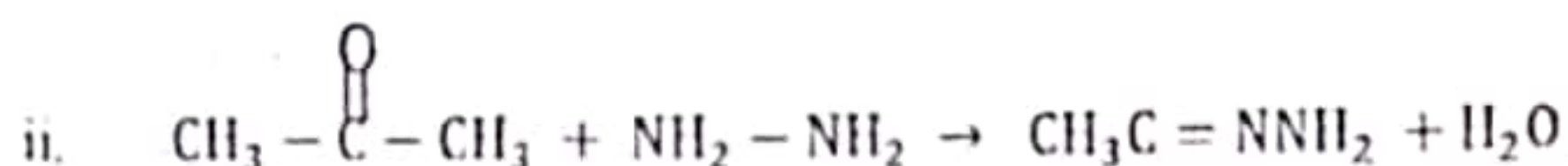
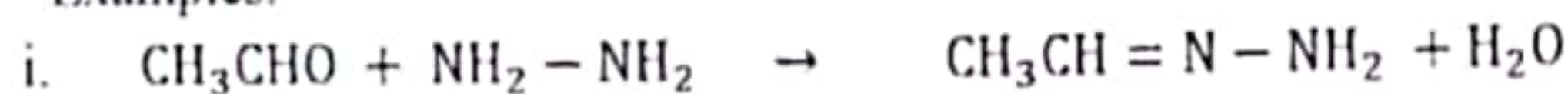
v. Reaction with hydrazine

Carbonyl compound reacts with hydrazine to form hydrazone.

Generally;

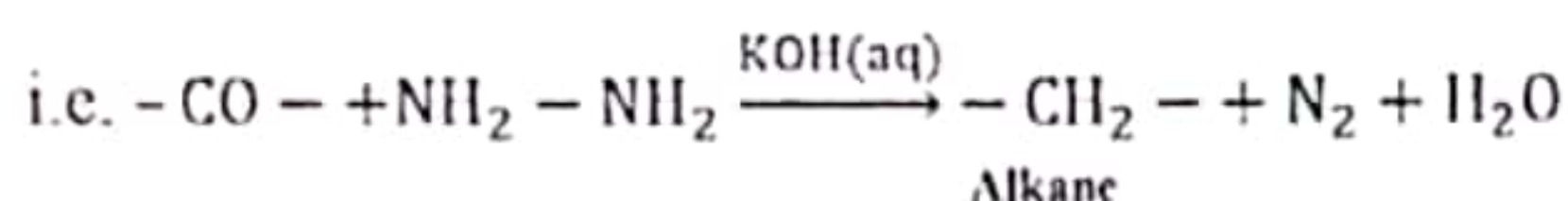


Examples:

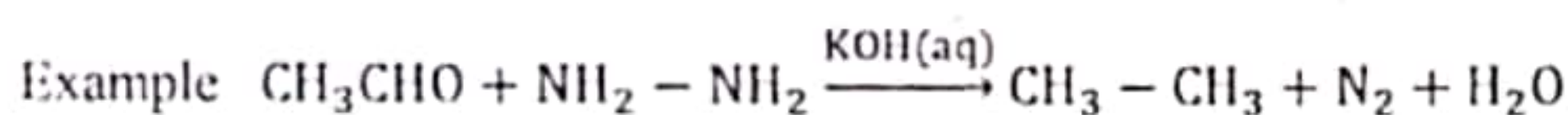
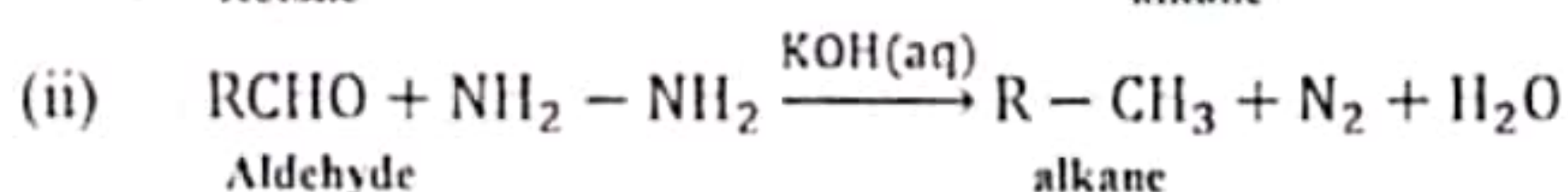
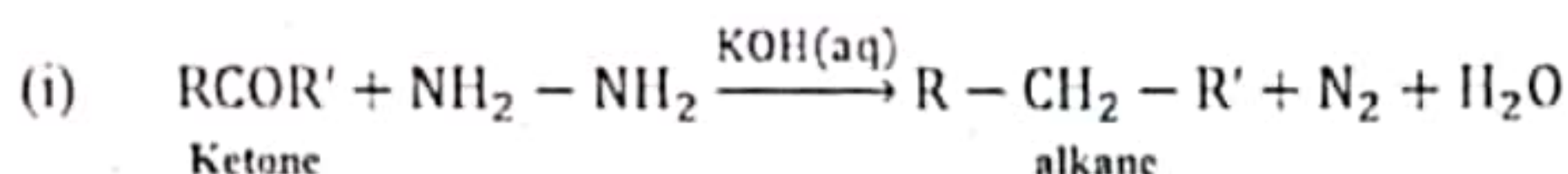


Be careful on conditions for the reaction!

Under presence of strong alkaline solution like KOH, carbonyl compounds reacts with hydrazine to give corresponding alkane and the reaction is known as **Wolff Kishner reduction**.

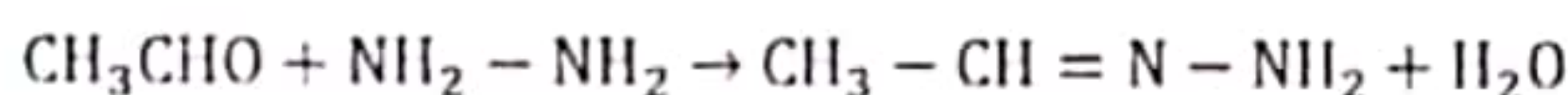


e.g.

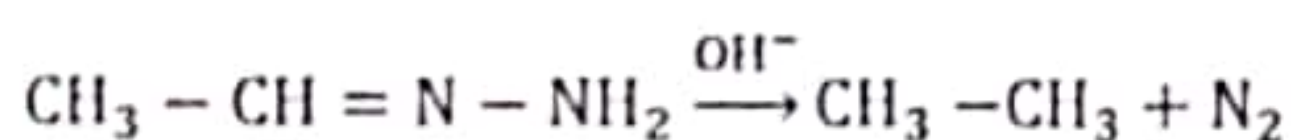


The reaction takes place in two steps:

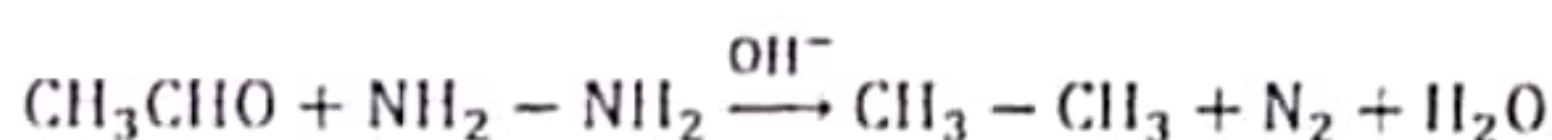
First step: Formation of hydrazone



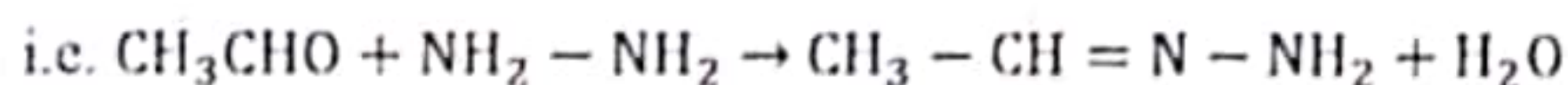
Second step: Formation of alkane



Whence the overall reaction becomes:



But in absence of alkaline medium, the final product becomes hydrazone.



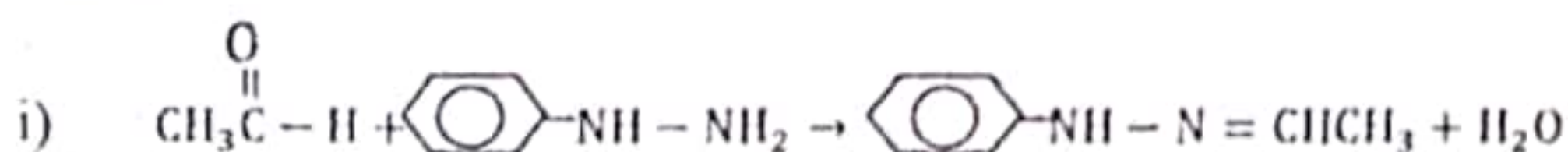
vi. Reaction with phenylhydrazine

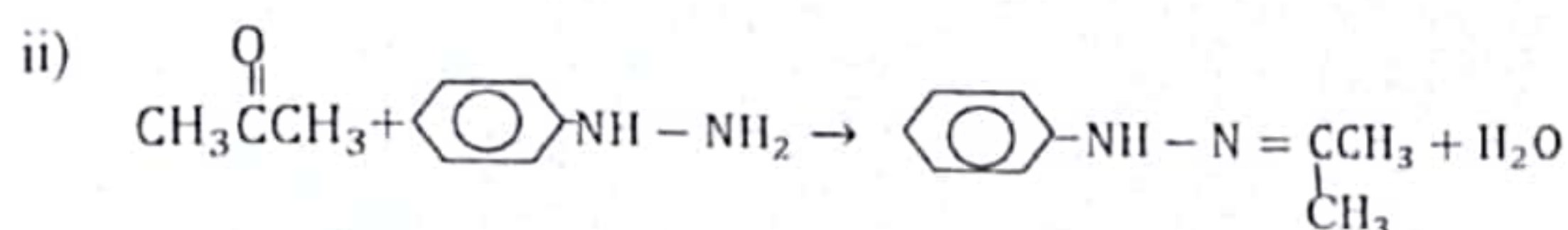
Carbonyl compound reacts with phenylhydrazine to form phenylhydrazone.

Generally;

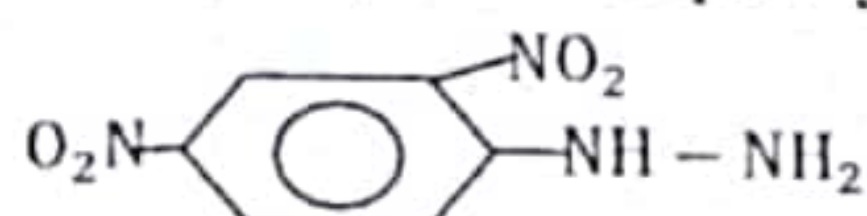


Examples:



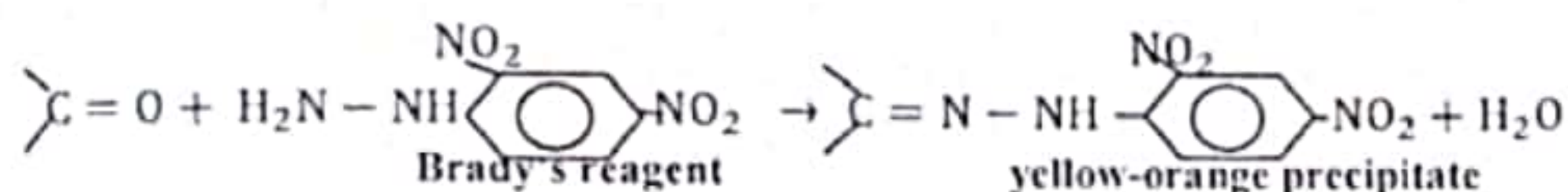


vii. Reaction with 2,4- dinitrophenylhydrazine (Brady's reagent)



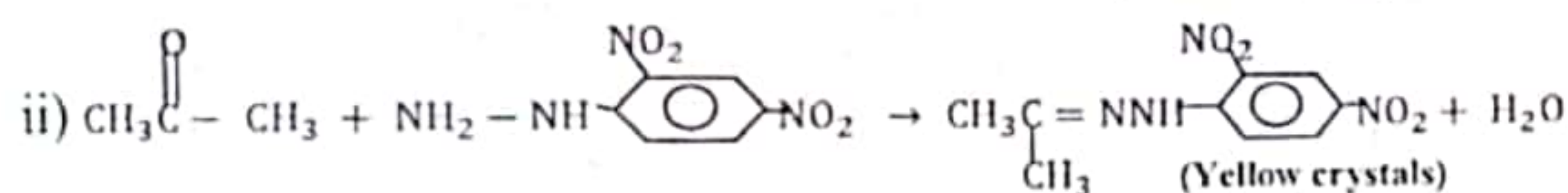
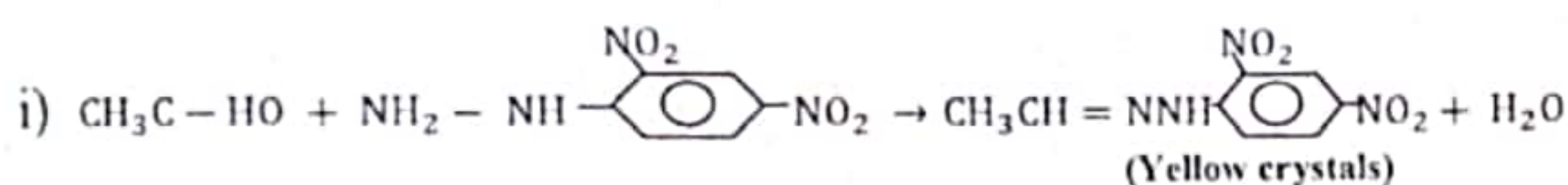
2, 4 -dinitrophenylhydrazine (Brady's reagent)

Carbonyl compound reacts with Brady's reagent to form yellowish crystalline product which appears as yellow-orange precipitate of 2,4- dinitrophenylhydrazone.



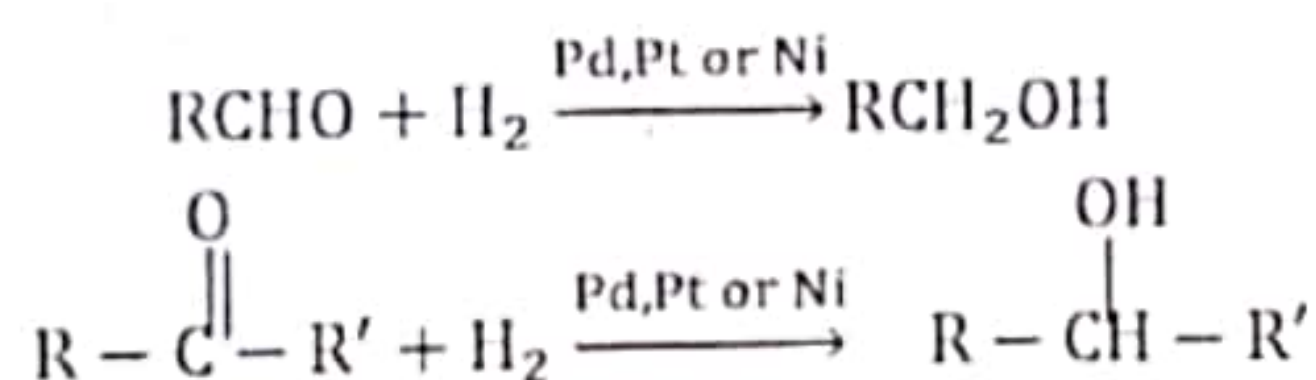
The reaction is used as a chemical test of presence of carbonyl group in the compound

Examples:



viii. Catalytic hydrogenation

On addition of hydrogen gas under presence of catalyst like finely divided platinum, nickel or palladium alcohol is formed



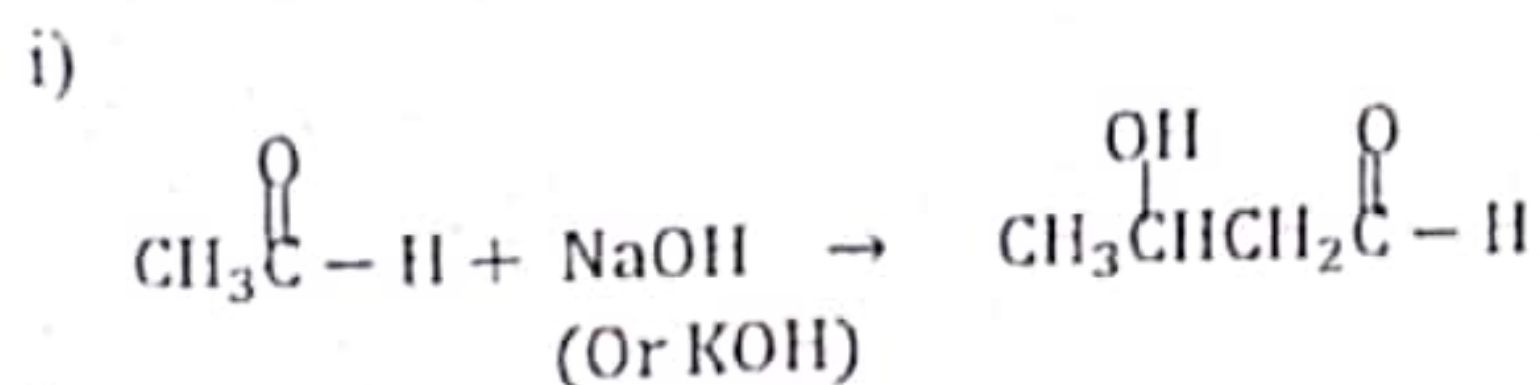
Other reactions of carbonyl compounds

Aldol-ketol condensation reaction

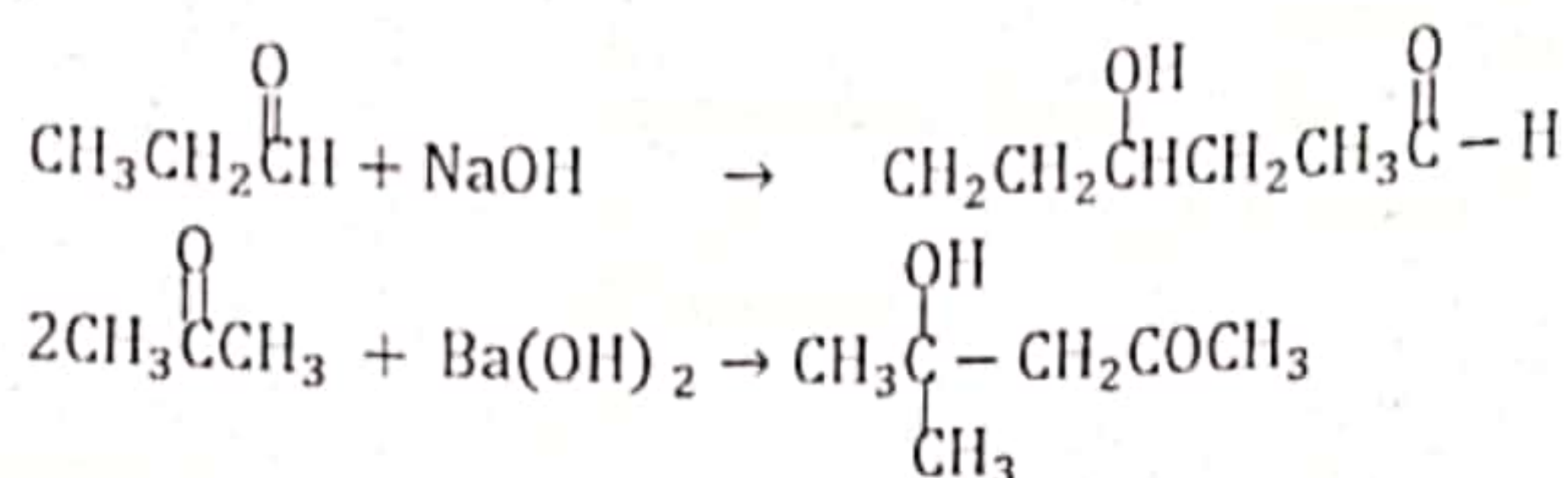
Aldol-ketol condensation reaction is the reaction between carbonyl compound with α -hydrogen and alkaline solution to form new compound which has both hydroxyl group and carbonyl group in the same compound.

Basically, **condensation reaction** is a reaction in which two or more molecules of the same or different compounds combine to form new compound with or without elimination of small molecules, like H_2O , HCl , alcohol etc.

Examples:

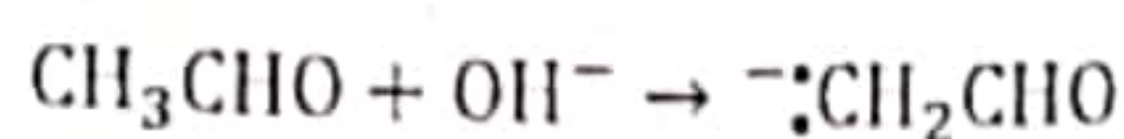


ii)



The reaction takes place in three steps as follows:

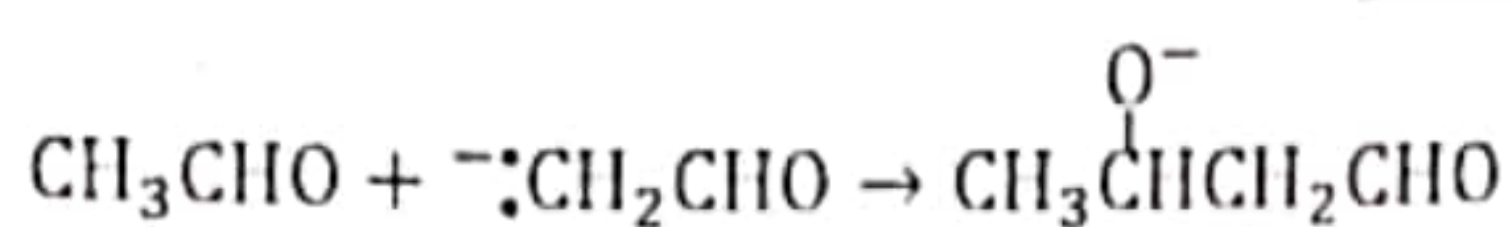
First step: Removal of α -hydrogen by base



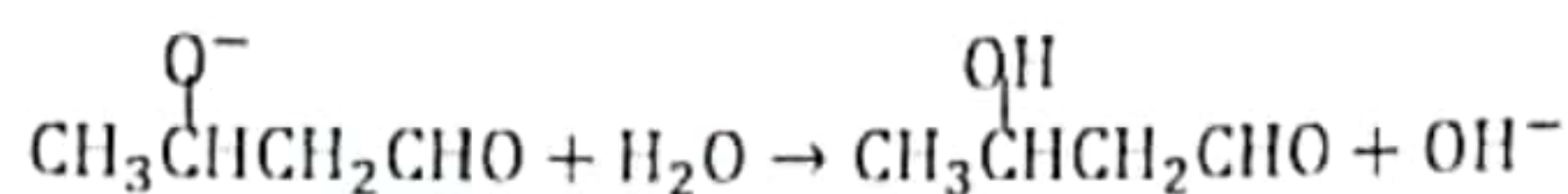
This reaction occurs due to acidic character of α -hydrogen. In absence of the α -hydrogen this step and thus the aldol condensation reaction will not occur.

Second step: Nucleophilic addition reaction of the aldehyde (ethanol) by the carbanion

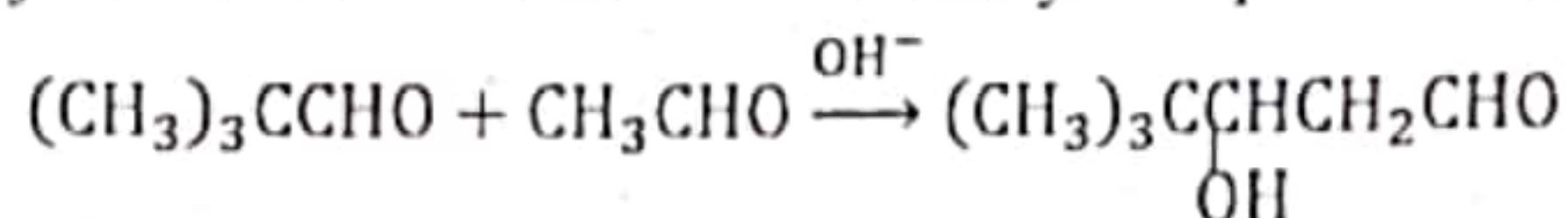
- This leads to the formation of the condensation product.



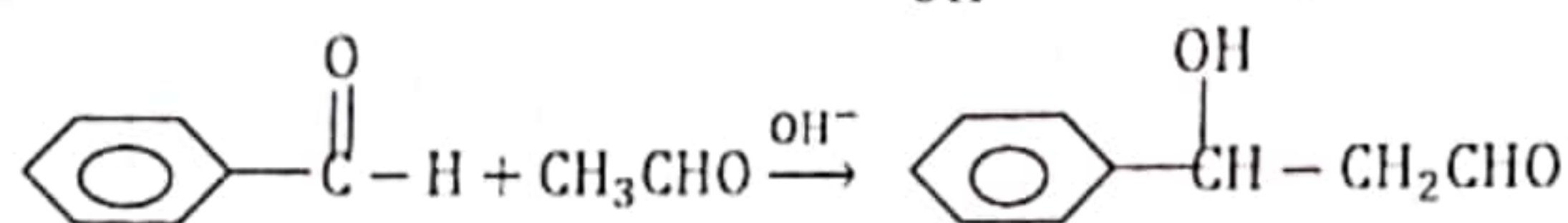
Third step: Protonation of the alkoxide ion by water and regeneration of catalyst (OH^-)



The reaction may occur even with different carbonyl compounds. For example;

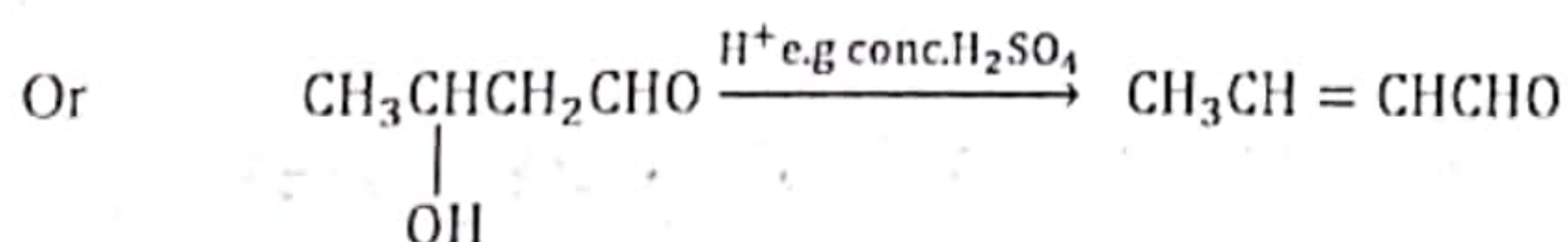
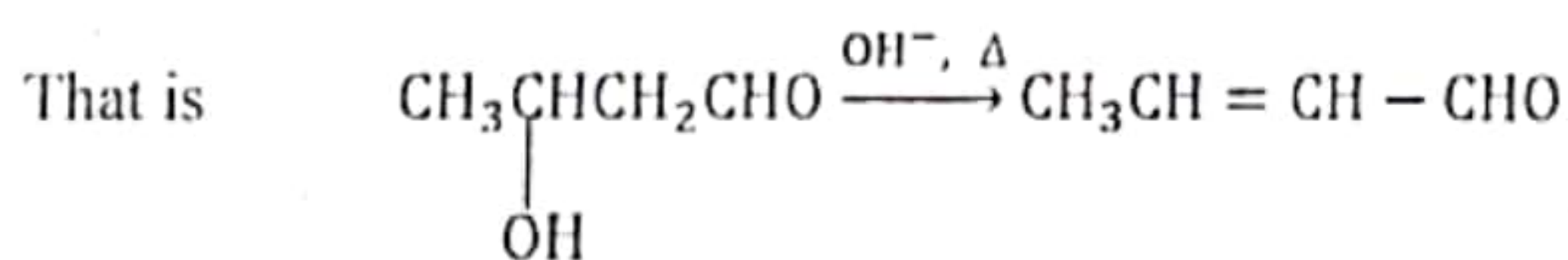


Or

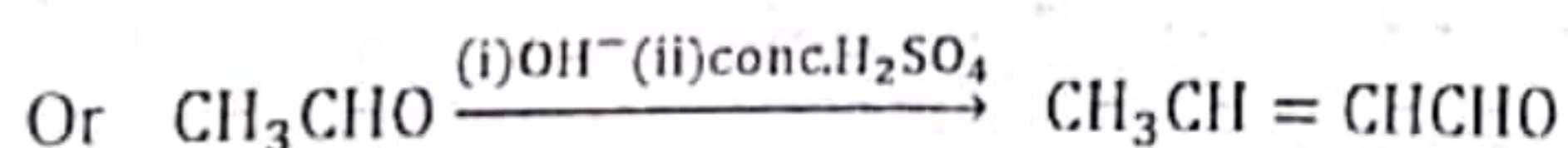
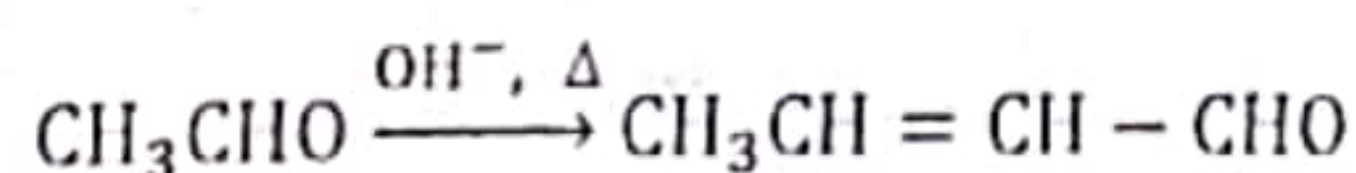


It should be understood that:

In presence of heated basic solution (or acidic medium) the aldol product can be dehydrated to give unsaturated aldehyde.



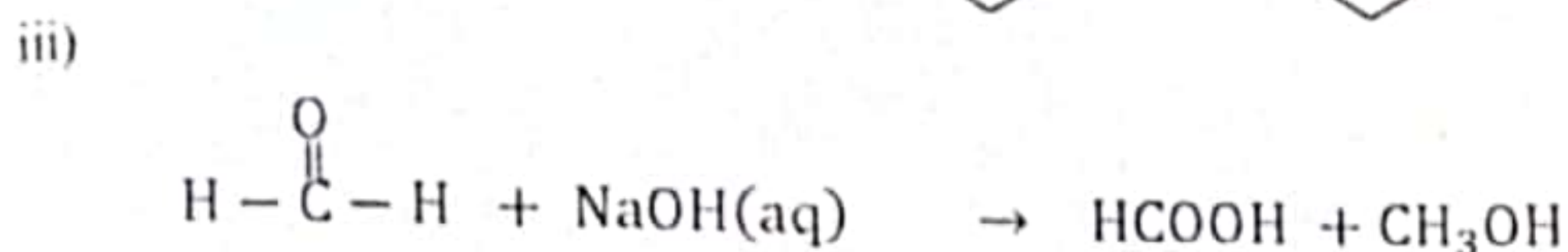
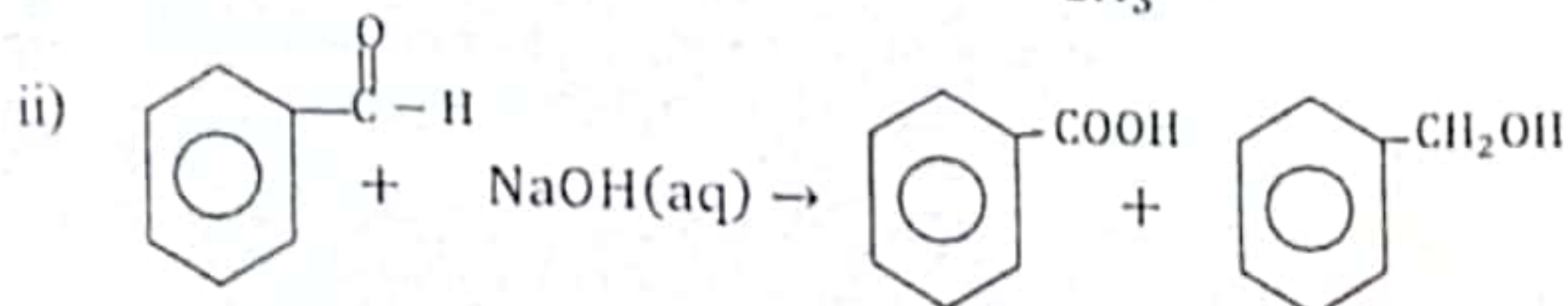
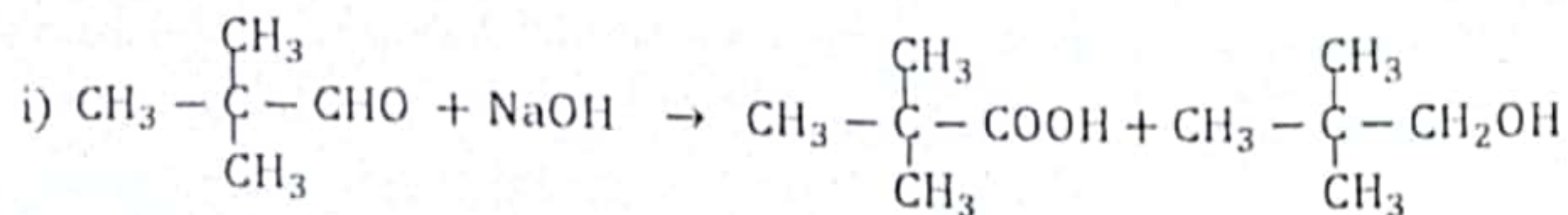
And therefore:



Cannizzaro reaction

This is the disproportionation reaction which occurs between carbonyl compound without α -hydrogen and alkaline solution to form carboxylic acid and alcohol.

Examples:

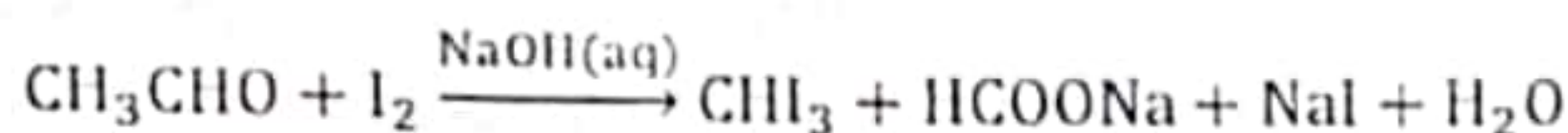


Iodoform test

This is the test for presence of terminal methyl group which is directly bonded to carbonyl group by giving yellow precipitate of iodoform, CHI_3 .

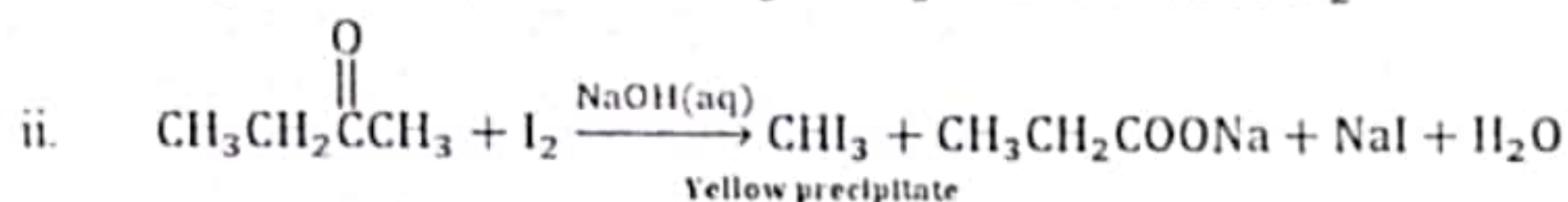
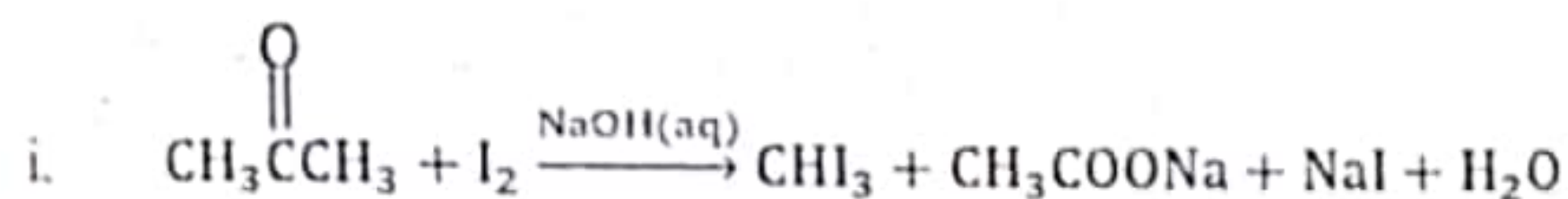
– For aldehydes, only ethanal give positive iodoform test.

i.e

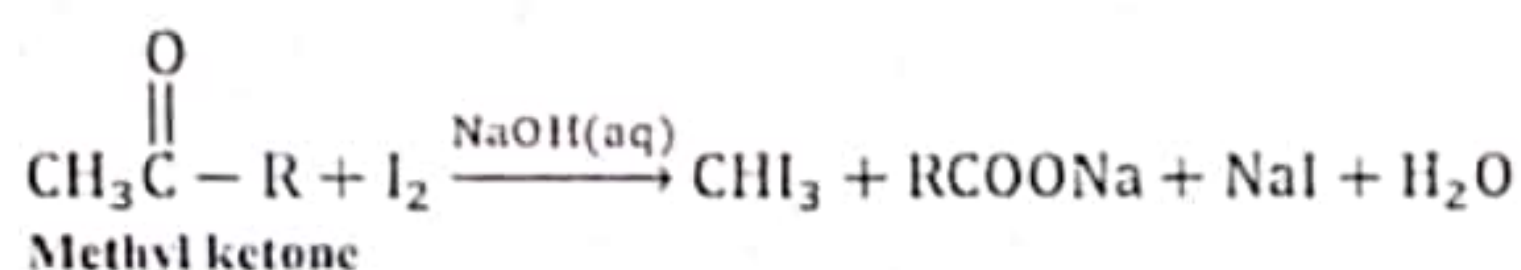


– For ketones; all methyl ketones (ketones with at least one methyl group which is directly bonded to carbonyl group) give positive test.

i.e



Generally;



CHEMICAL TESTS TO DISTINGUISH BETWEEN ALDEHYDES AND KETONES

Aldehyde and ketone may be distinguished using the fact that aldehyde is good reducing agent i.e it can be oxidised easily while ketone cannot be oxidised.

There are two solutions which are commonly used to distinguish aldehydes and ketones.

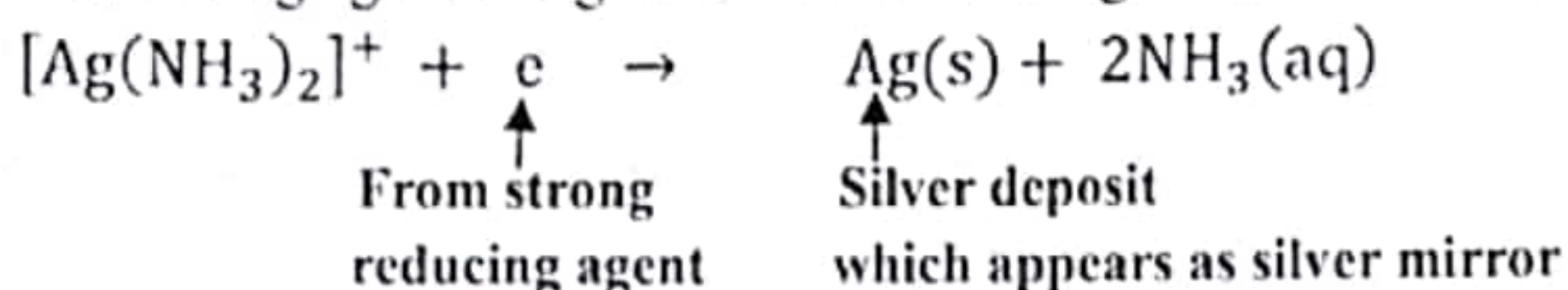
- Tollen's reagent which consist of $[\text{Ag}(\text{NH}_3)_2]^+$ (silver mirror test)
- Fehling's / Benedict solution which consist of Cu^{2+}

By using Tollen's reagent (silver mirror test)

Tollen's reagent is the ammonical silver nitrate.

– It contains complex cation $[\text{Ag}(\text{NH}_3)_2]^+$

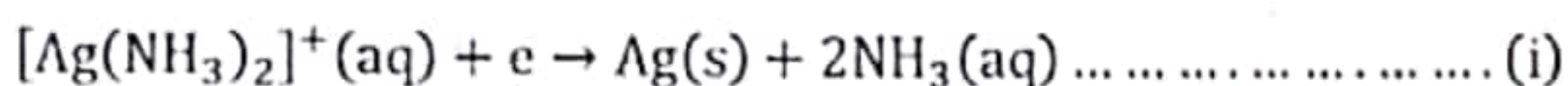
- It is mild oxidizing agent and get oxidised according to the following equation



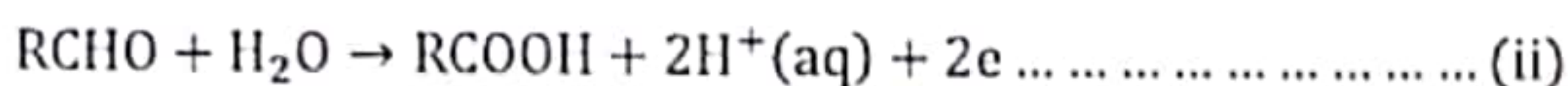
Thus Tollen's reagent can reduce aldehyde to carboxylic acid while itself becomes oxidised to silver.

That is;

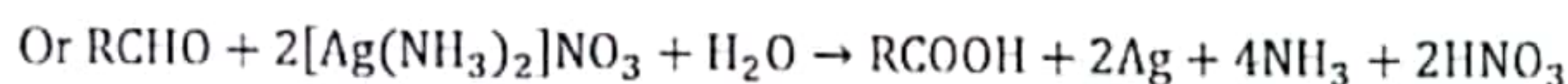
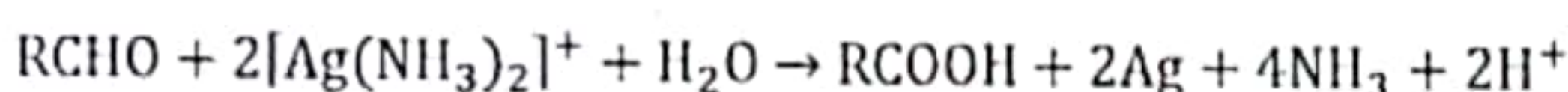
Reduction a half reaction:



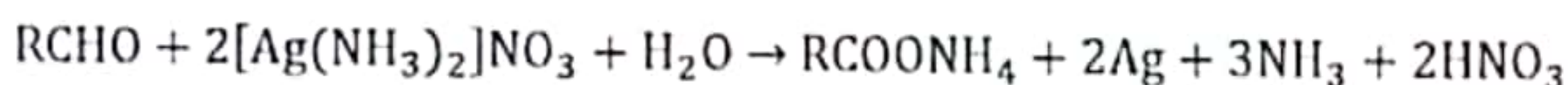
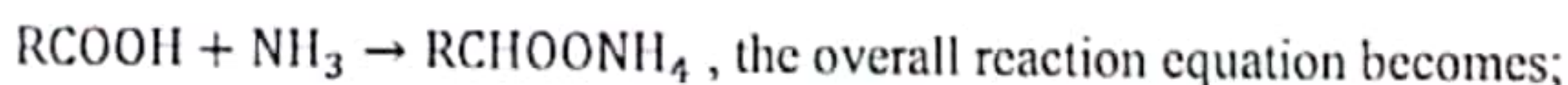
Oxidation a half reaction;



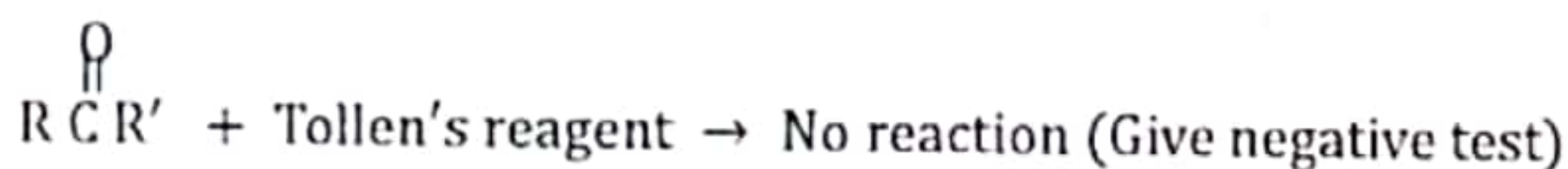
And the overall reaction becomes (Is obtained by taking 2(i) + (ii))



And the if there is a further reaction between RCOOH and NH₃ as per equation;



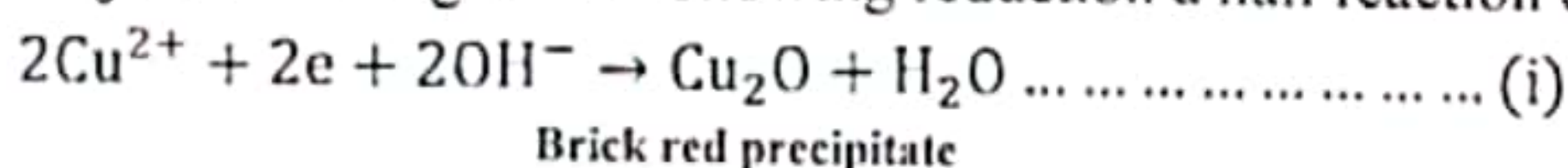
While



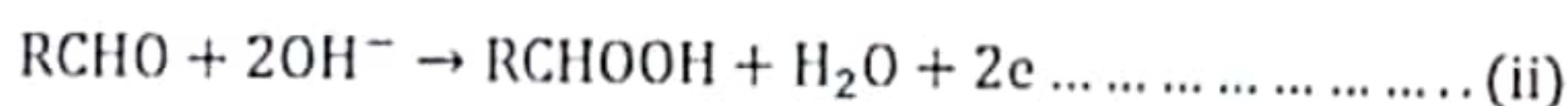
By using Fehlings /Benedict solution

Fehling's solution is alkaline solution containing Cu²⁺ ions.

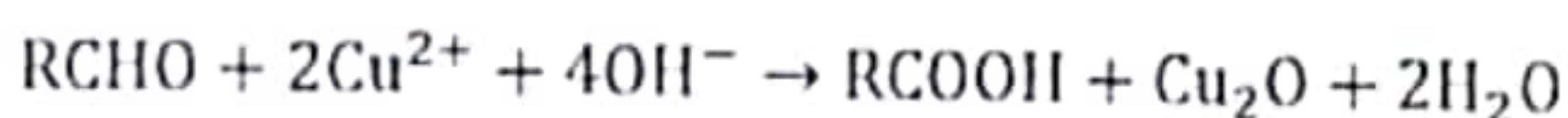
- Like Tollen's reagent, it is a mild oxidizing agent and can be oxidised by strong reducing agent like aldehyde according to the following reduction a half reaction equation;



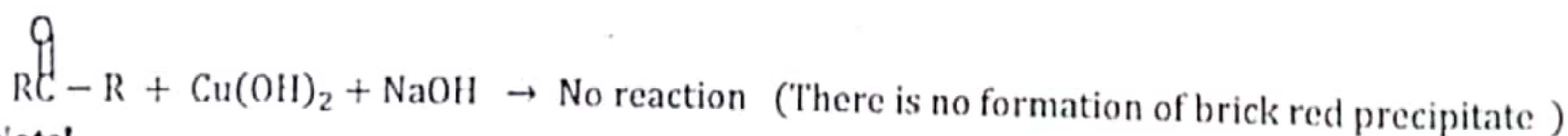
While aldehyde become oxidised to carboxylic acid according the following oxidation a half reaction equation;



And the overall reaction equation becomes (by taking (i) + ii)

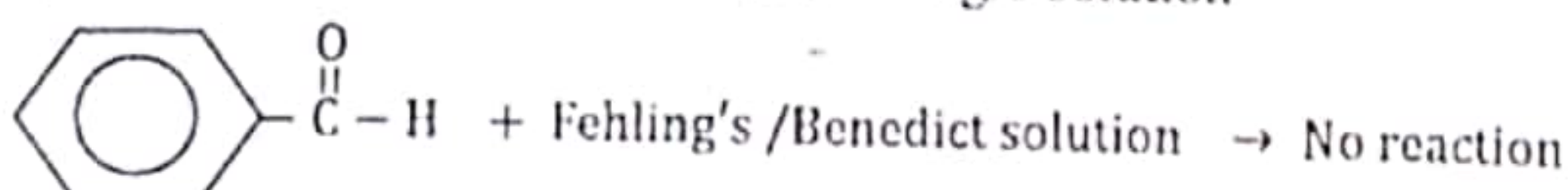


But



Note!

Benzaldehyde does not react with Benedict/Fehling's solution



It's good to understand that: Compared to alcohols aldehydes are stronger reducing agents (they are oxidised easily to carboxylic acid)

- So unlike aldehydes, alcohols cannot reduce either Fehling's or Tollen's reagent.

Alcohol + Fehling's solution → No reaction

Alcohol + Tollen's reagent → No reaction

Example 5

Compound **A** which has an unbranched carbon chain, react with methyl magnesium bromide to give after hydrolysis compound **B**. Chromic acid oxidation of **B** gives **C** ($C_5H_{10}O$) which gives crystalline product with 2, 4-dinitrophenylhydrazine and a positive iodoform test.

- Give formula of **A**, **C** and equation for all reactions mentioned.
- Give the formula of possible isomer of **A** that would give the same result as **A** in the above transformation.

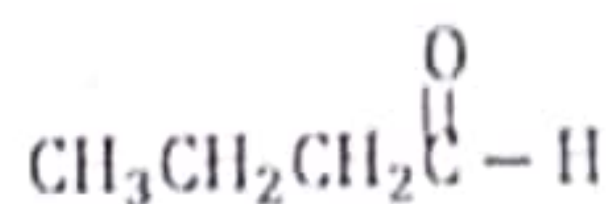
Solution

- Molecular Formula $C_5H_{10}O$ confirm general molecular formula of $C_nH_{2n}O$
- Thus **C** is either aldehyde, ketone or unsaturated alcohol with $C = C$
- Formation of crystalline product with 2,4-dinitrophenylhydrazine confirm that there is carbonyl group in **C**; this insist that **C** is either aldehyde or ketone and not alcohol
- Since **C** gives positive iodoform test there is terminal methyl group which is directly bonded to carbonyl group in **C** i.e. **C** must be methyl ketone (the only aldehyde which give positive iodoform test is ethanal which has two carbon atoms and not 5 as given).
- A compound which gives ketone on oxidation is secondary alcohol.
- Thus **B** must be 2° alcohol.
- Carbonyl compound which give secondary 2° alcohol with grignard reagent (in this case methyl magnesium bromide) are higher member of aldehyde rather than methanal (ketone give 3° alcohol) which give 1° alcohol.

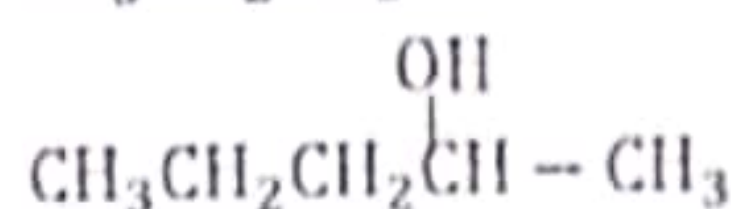
Thus **A** is higher member of aldehyde with number of carbon atoms greater than one.

- Product formed after reaction between methyl magnesium bromide followed by hydrolysis indicates that there are 4 carbons in **A**.
- So **A** must be aldehyde with 4-carbons and **B** must be 2° alcohol with 5 carbons.
- Since **A** is unbranched:

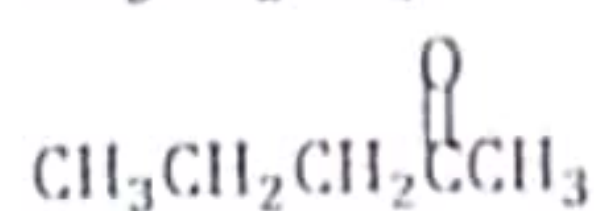
Structual formula of **A**



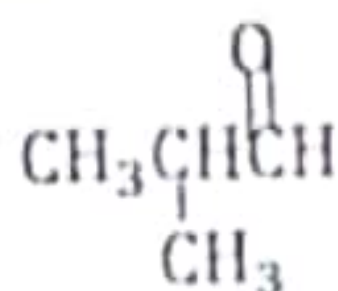
Stuctual formula of **B**



Structure formular of **C**



- Possible isomer with the same results as that of **A** is



USES OF CARBONYL COMPOUNDS

(i) As a organic solvent

Mainly acetone (propanone) is used for this purpose.

- It is used as solvent in adhesives, paints, cleaning solvents, nail polish and nail polish remover.
- Butanone is also important industrial solvent.

(ii) In perfume industrial

- Mainly benzaldehyde is used for this purpose

(iii) In manufacture of dyes

- Some dyes like malachite green are manufactured from benzaldehyde.

(iv) In synthesis of other organic compound

Carbonyl compounds (mainly benzaldehyde, methanal and ethanal) are commonly used in the preparation of other organic compounds.

- Benzaldehyde can be used in synthesis of compounds like benzoylchloride and toluene
- Ethanol can be used in the preparation of ethanoic acid, butanol and ethyl ethanoate
- Methanal is very useful in the manufacture of various polymers like Bakelite

(v) As disinfectant, germicide and insecticide

Mainly methanal (formalin) is used for this purpose.

- It commonly used in preserving biological samples
- Also it used:
 - To activate bacterial products for **toxoid vaccines** (vaccine that uses an inactive bacteria toxin to produce immunity).
 - To kill unwanted viruses and bacteria that might contaminate the vaccine during production.
 - To kill fungi
 - In treatment of urinary tract infections (UTI)
- This is done through derivative of methanal (However this is not safe for long term use because formaldehyde may cause cancer)

(vi) Silvering mirror

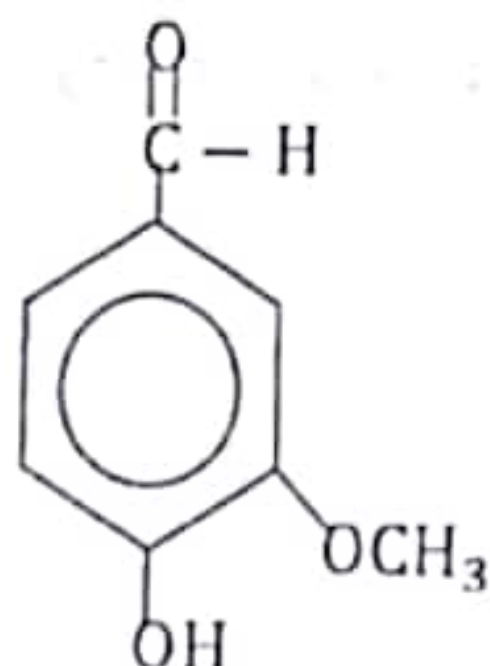
Aldehydes (mainly ethanal) are used for this purpose.

- Process employ the reaction between ethanal and Tollen's reagent as explained in the silver mirror test.

(vii) As artificial and natural additives to food

Many aldehydes and ketones are important to food industry in which they are used as artificial and/or natural additives.

- **Vanillin** is the derivative of benzaldehyde which is the principal component of natural **vanilla**.



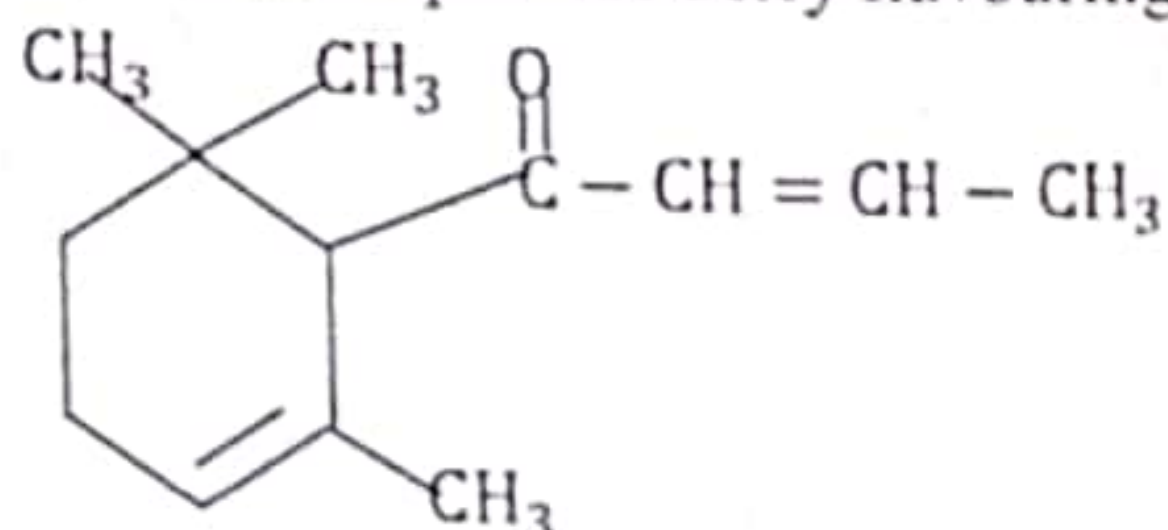
Vanillin (It is naturally found in the vanilla beans)

(Artificial vanilla flavouring is a dilute solution dissolved in ethanol)

- 2 – octanone (ketone) used to provide mushroom flavouring in the food industry



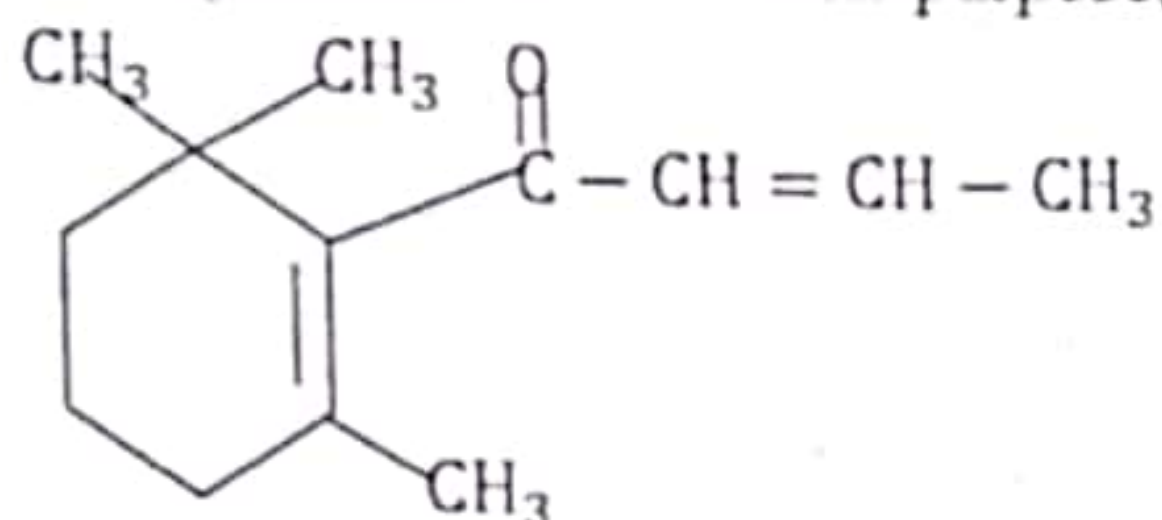
- α -demascone (ketone) is used to provide berry flavouring



Common name: α -demascone

IUPAC name: 1-(2,6,6-trimethyl-2-cyclohexenyl)but-2-en-1-one

- β -demascone (ketone) may be used for the same purpose (like that of α -demascone)



Common name: β -demascone

IUPAC name: 1-(2,6,6-trimethyl-1-cyclohexenyl)but-2-en-1-one

(α and β -demascones are used in deodorant spray, shampoo and soap as they have sweet rose odour).

HAZARDS OF CARBONYL COMPOUND

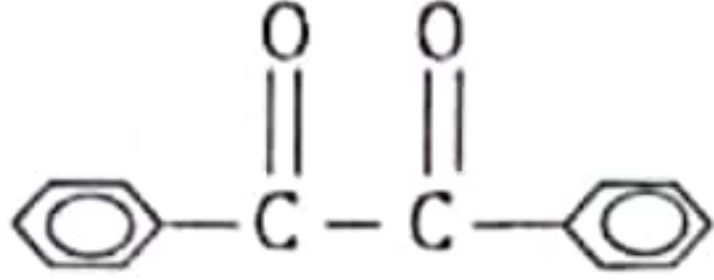
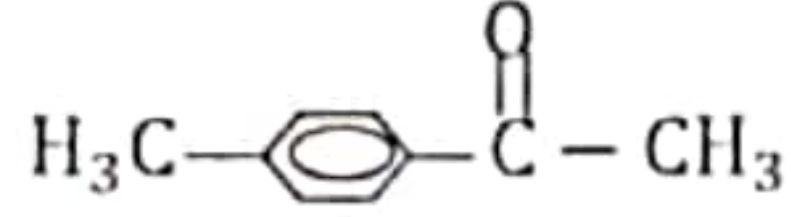
This includes the following:

- **They are inflammable**
 - This is major problem associated with methanal and ethanal (to smaller extent); these compounds are volatile and easily inflammable. (Generally flammability of aldehyde decreases with an increase in length of carbon chain)
- **Chemical burn**
 - Are irritating to the eyes, nose and throat (this occurs mainly for methanal).
- **Respiratory and allergic effect.**
 - This occurs when there is prolonged exposure to methanal.
 - People with asthma are particularly susceptible to exposure to these products that may aggravate their symptoms.
 - Also the aldehydes may cause occupational asthma for those working in prolonged contact with these products
- **They are carcinogenic compounds.**
 - Some carbonyl compounds may cause cancer.

PRACTICE EXERCISE 19

Problem 1

Give systematic names of the following organic compounds:

- i. HCHO
- ii. $\text{CH}_2 = \text{CH} - \overset{\text{O}}{\parallel}\text{C} - \overset{\text{O}}{\parallel}\text{C} - \text{H}$
- iii. 
- iv. 
- v. $\text{H} - \overset{\text{O}}{\parallel}\text{C} - \overset{\text{O}}{\parallel}\text{C} - \text{H}$

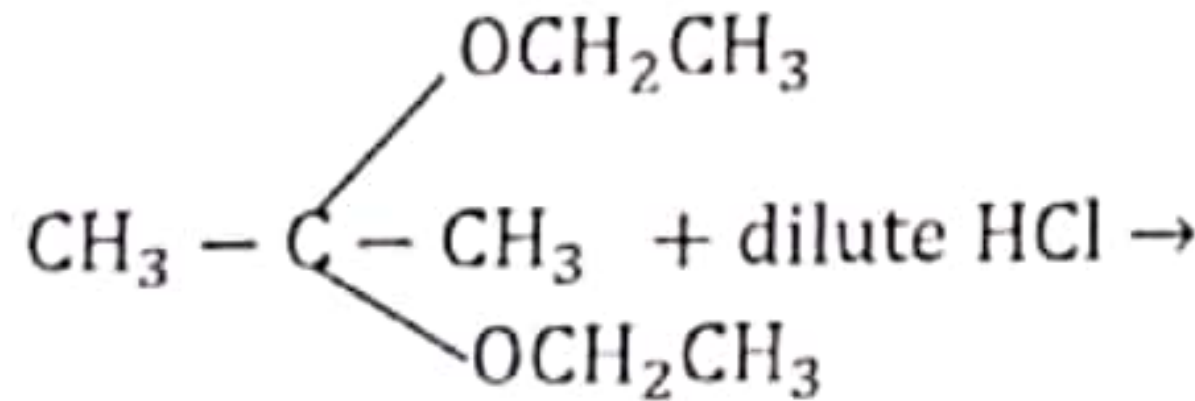
Problem 2

Write chemical equation to show preparation of:

- i. Propanone from an alkene
- ii. Propanone from a carboxylic acid
- iii. Ethanol from but-2-ene
- iv. Phenylethanone from benzene
- v. Propanal from nitrile

Problem 3

Complete the following organic reactions:

- i. $\text{C}_6\text{H}_5\text{CHO} + \text{KCN} \xrightarrow{\text{Alcohol}}$
- ii. $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5 + \text{NaHSO}_3 \rightarrow$
- iii. $\text{CH}_3\text{COCH}_3 + \text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH} \xrightarrow{\text{HCl(g)}}$
- iv.  + dilute HCl $\rightarrow$
- v. $\text{CH}_3\text{COCH}_3 + \text{N}_2\text{H}_4 \xrightarrow{\text{KOH(aq)}}$
- vi. $\text{CH}_3\text{CHO} + \text{CH}_3\text{C} \equiv \text{CH} \rightarrow$

Problem 4

List down at least five uses of carbonyl compounds

Problem 5

List down at least three hazards of carbonyl compounds

Chapter 20

CARBOXYLIC ACIDS

These are organic compounds with carboxylic group – COOH as functional group.

- They can be aliphatic or aromatic
- They have general molecular formula of $C_nH_{2n}O$

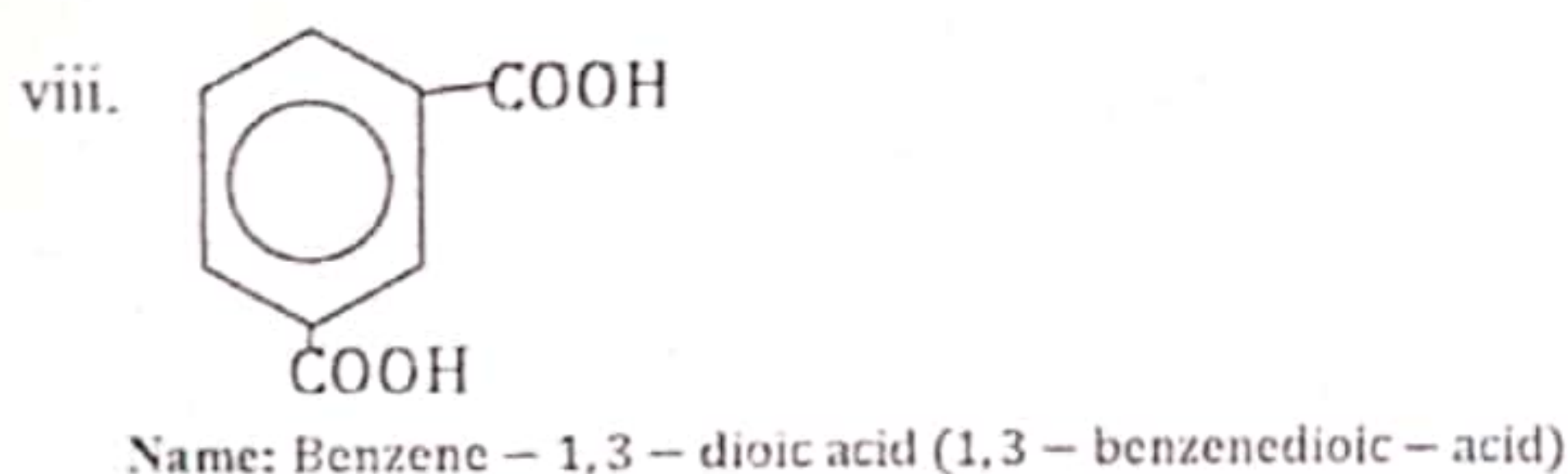
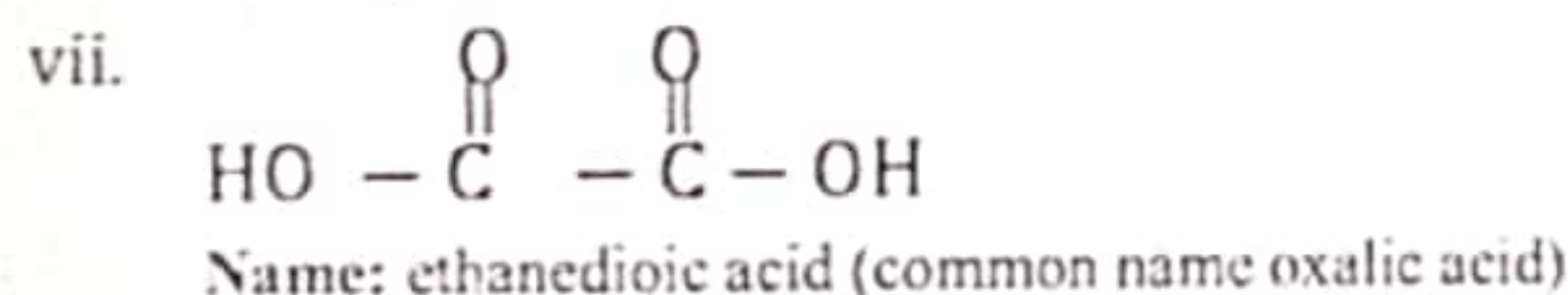
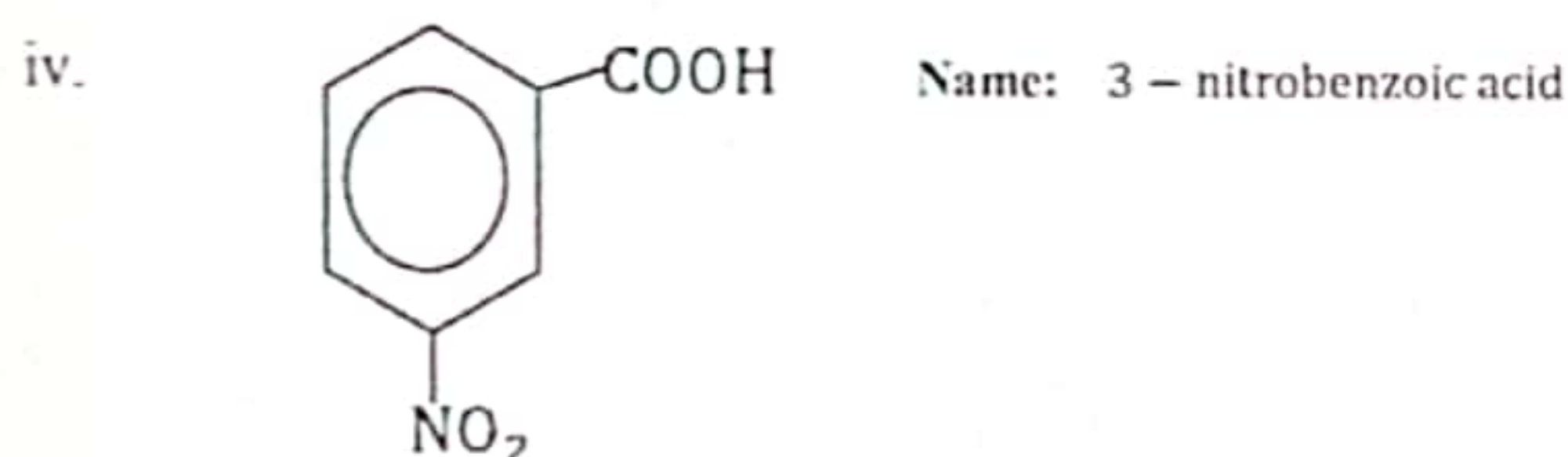
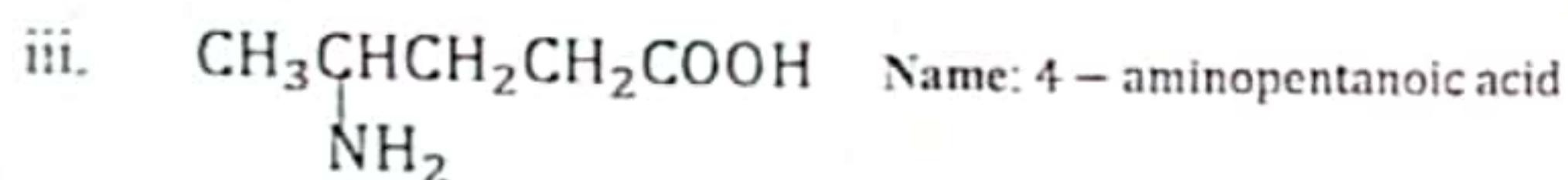
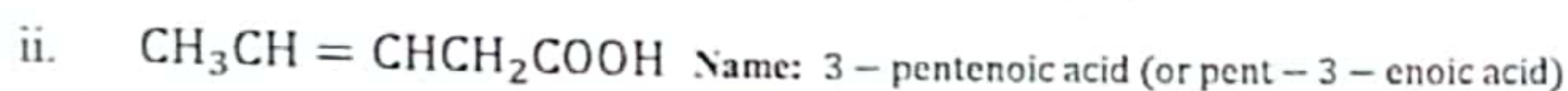
Carboxylic group, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$ result after mixing carbonyl group and hydroxyl group

NOMECLATURE OF CARBOXYLIC ACIDS

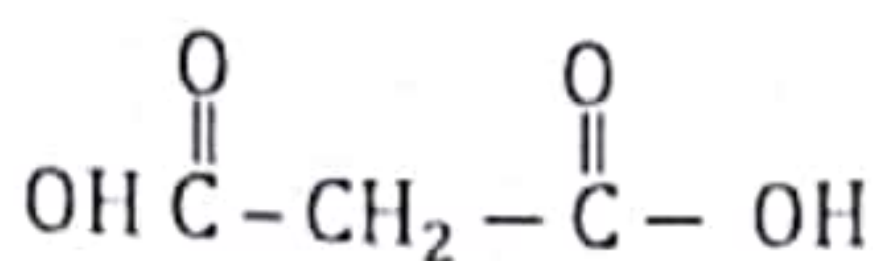
Rules of naming carboxylic acids are similar to those of naming other organic compounds with the following modifications;

- The parent chain must contain carboxylic group.
- In numbering carbon atoms, a carbon in carboxylic group must be given first position.
- Naming carboxylic acid is done by leaving letter 'e' from corresponding name of the hydrocarbon then add (replace it with) – oic acid.

Examples:



ix.



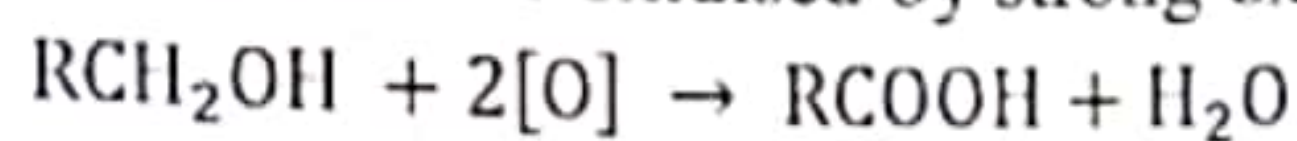
Name: Propane - 1, 3 - dioic (simply: propanedioic acid)

PREPARATIONS OF CARBOXYLIC ACID

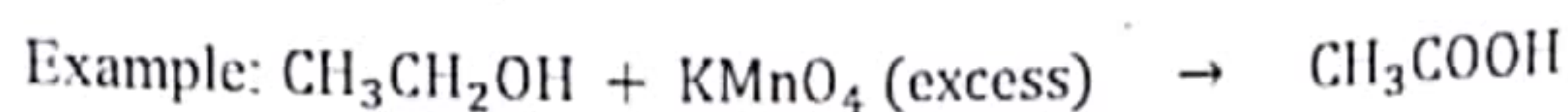
Oxidation

i) Oxidation of alcohol

Alcohol can be oxidised by strong oxidizing agent like $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 to give carboxylic acid.



Where $[\text{O}]$ are oxygen atoms from strong oxidising agent



If oxidizing agent is weak or in limited amount aldehyde is formed.

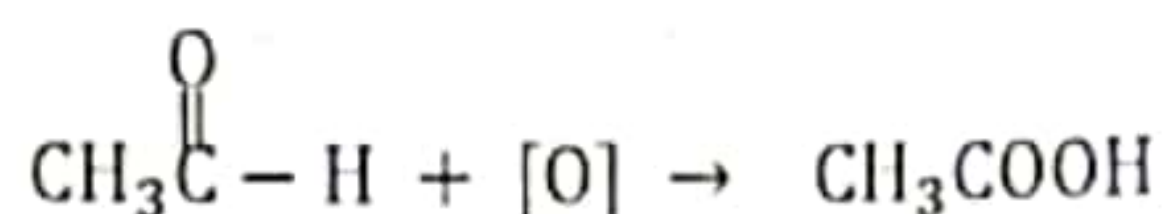
ii) Oxidation of carbonyl compound

Aldehyde can be oxidised easily to give carboxylic acids. i.e

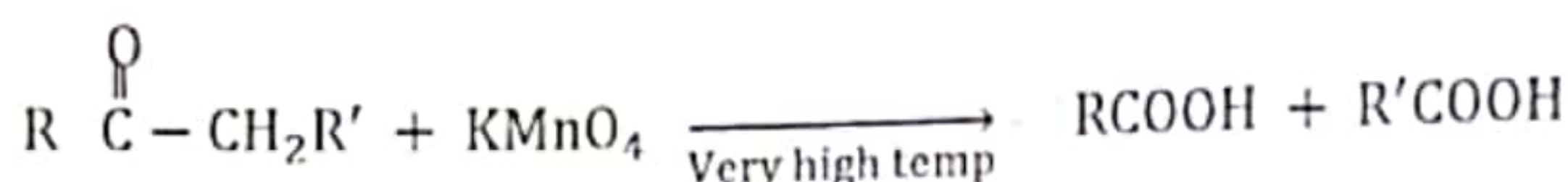


Where $[\text{O}]$ is oxygen atom from strong oxidizing agent like $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4

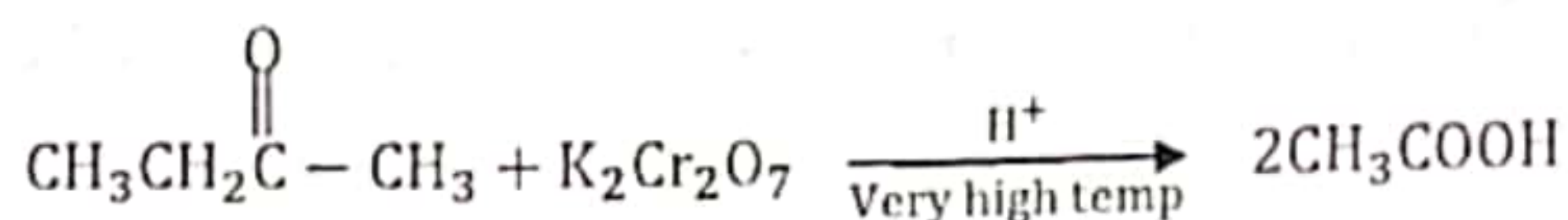
Example



Ketones resist oxidation but under drastic (vigorous) condition can form carboxylic acid.



Example



(However under normal condition there is no chemical reaction between ketone and oxidising agent)

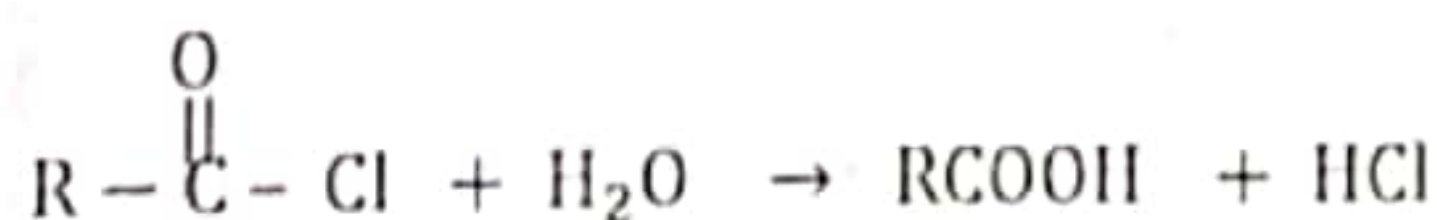
Note that:

Methanoic acid can not be prepared by this method (oxidation method). Since it can further be oxidised to CO_2 and H_2O .

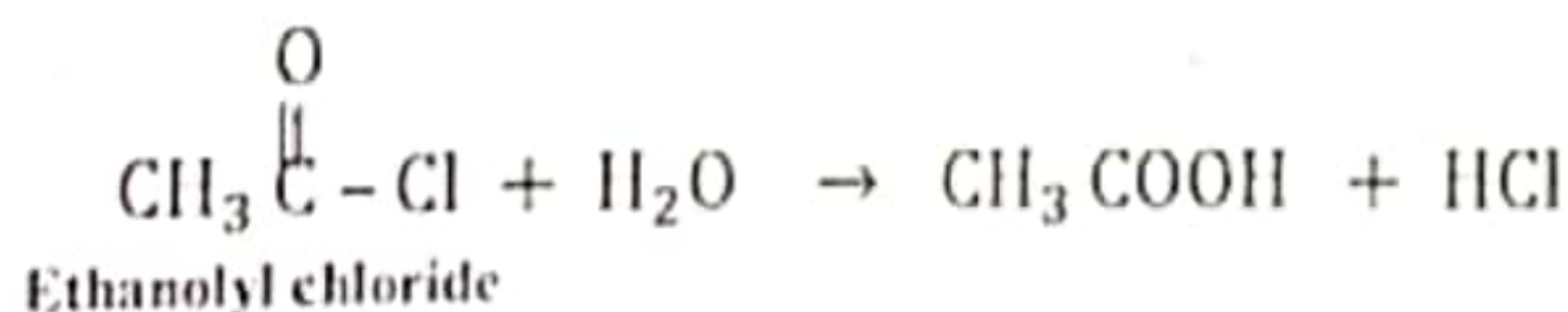
Hydrolysis

a) Hydrolysis of acyl compounds

Generally;

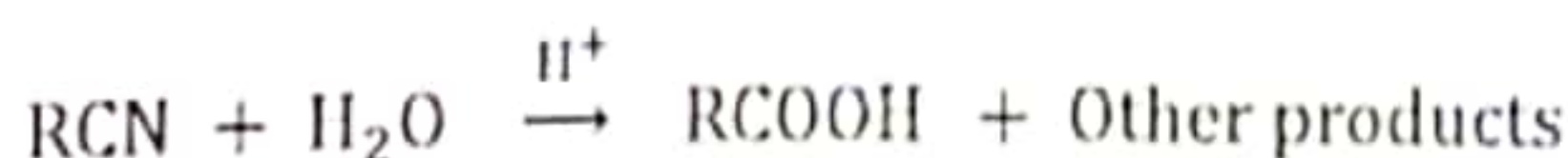


Example,



b) Acidic hydrolysis of nitrile

Generally;

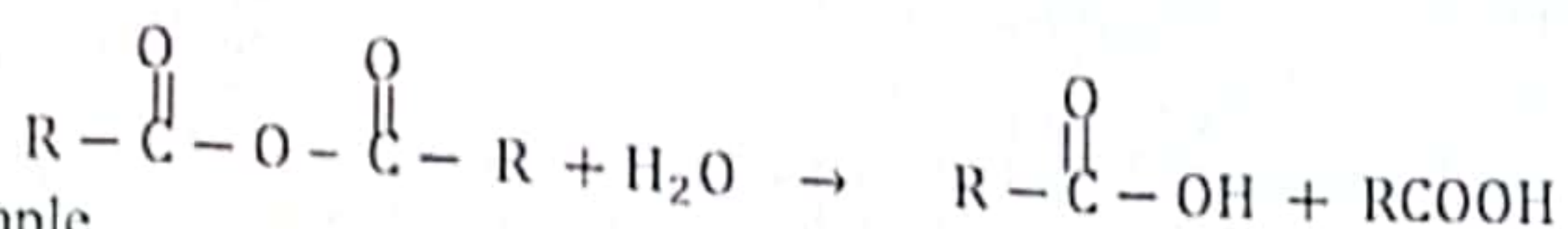


Example,

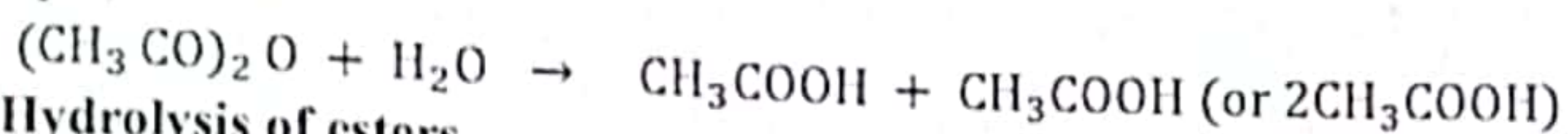


c) Hydrolysis of acid anhydride

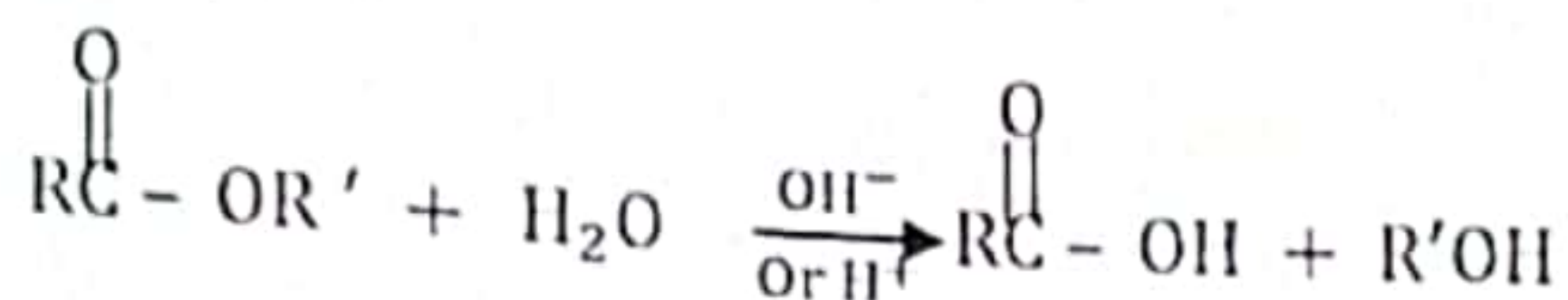
Generally;



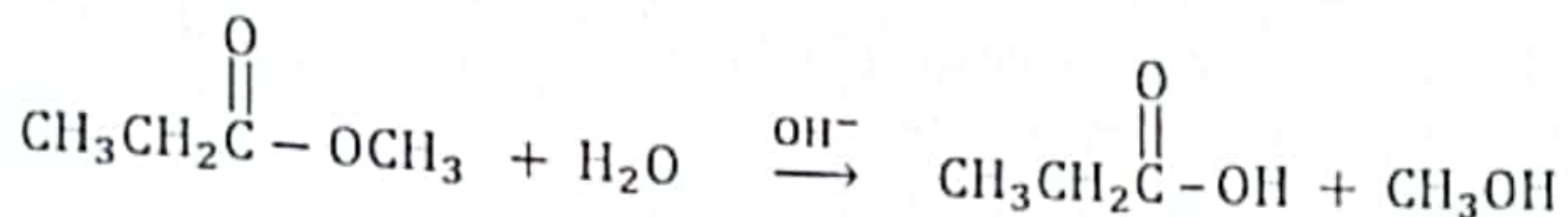
Example,



d) Hydrolysis of esters



Example,



Why OH^- (basic medium) is preferred to H^+ (acidic medium)?

Reason:

Because under H^+ , the reaction will be reversible, i.e cannot reach into completion. This is because esterification is done under presence of concentrated H_2SO_4 (acidic medium) and above products (carboxylic acid and alcohol); so in this case the product formed will have low percentage yield of carboxylic acid as compared to the product formed under presence of OH^- (basic medium).

e) Acidification of carboxylic salts

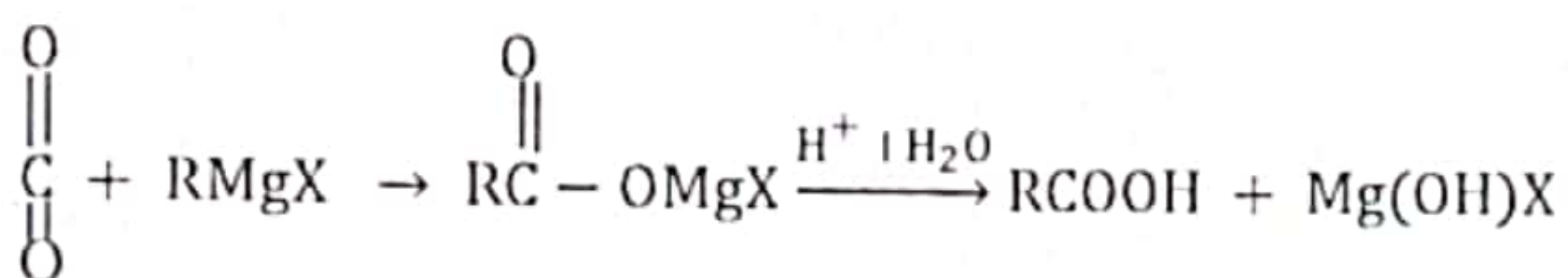
Carboxylic acid can be prepared by reacting carboxylic salt like sodium carboxylate with acidic solution like hydrochloric acid.

That is $RCOONa + HCl(aq) \rightarrow RCOOH + NaCl$

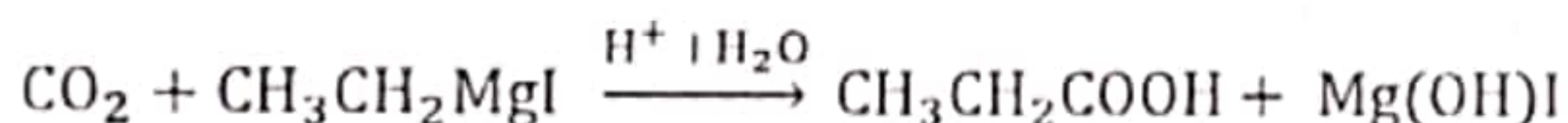
From Grignard reagent

Carbondioxide react with Grignard reagent followed by acidic hydrolysis to form carboxylic acid.

Generally;



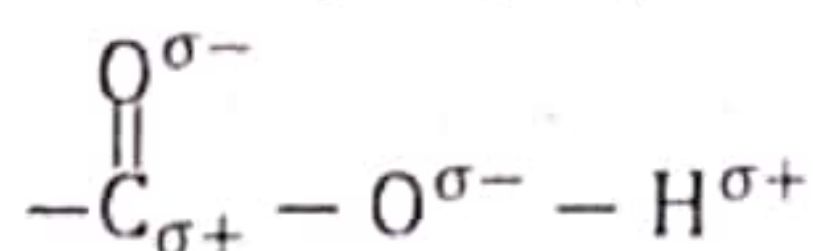
Example,



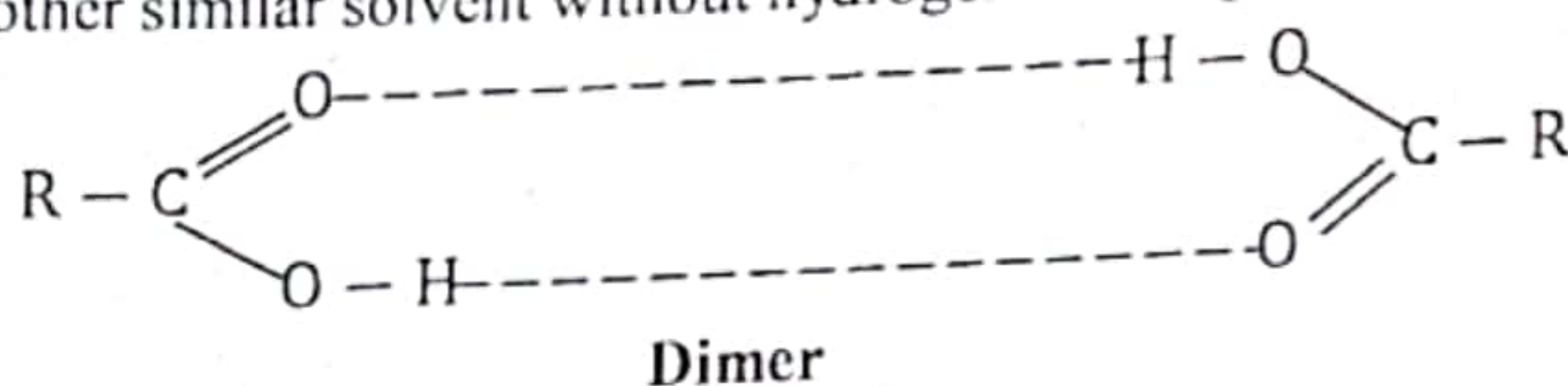
PHYSICAL PROPERTIES OF CARBOXYLIC ACID

- Carboxylic acid has highest **boiling point** among alcohol, phenol, carbonyl compounds or any other hydrocarbons with comparable molecular weight due to stonger hydrogen bonding existing between molecules of carboxylic acid.
- Carboxylic acid are more **soluble** in water than either alchol, phenol, carbonyl compound or any other hydrocarbons because they are capable of making stronger hydrogen bonding with water molecules and high polarity of carboxylic group.

i.e.



- Carboxylic acid is capable of undergoing **dimerisation** when it is in the hydrocarbon solvent or any other similar solvent without hydrogen bonding.



- Carboxylic acids are **acidic** in nature.
- Compared to alcohols, carboxylic acids are stronger acids due to presence of mesomerism which makes it easier for O-H to break so as to release H^+ and also stabilise the carboxylate ion ($RCOO^-$) which is formed after releasing the H^+ .
- Compared to phenol, carboxylic acid is stronger acid because its carboxylate ion has stronger mesomerism than phenoxide ion whereby the negative charge in the carboxylate is shared through mesomerism by two strong electronegative oxygen atoms while in phenoxide ion there is only one oxygen atom. Furthermore the extra oxygen atom in the carboxylic group exerts negative inductive effect.
- Compared to aliphatic carboxylic acid, benzoic acid is stronger acid because the benzene ring can withdraw electrons by negative inductive effect (Remember; carbons in benzene are sp^2 hybridised and therefore they have greater percentage of s-character than sp^3 hybridised carbon in alkyl group of aliphatic carboxylic acid and hence are more electronegative).
- So while phenyl group in benzoic acid exerts negative inductive effect to carboxylic group, alkyl group in aliphatic carboxylic acid exerts positive inductive effect and hence benzoic acid is stronger acid than aliphatic carboxylic acid like ethanoic acid.

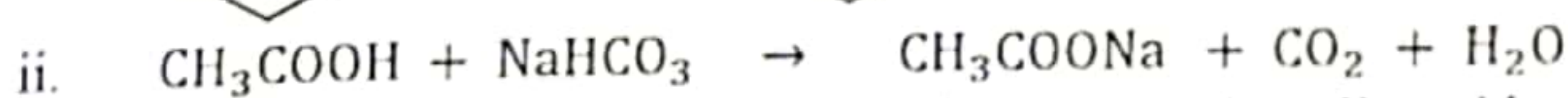
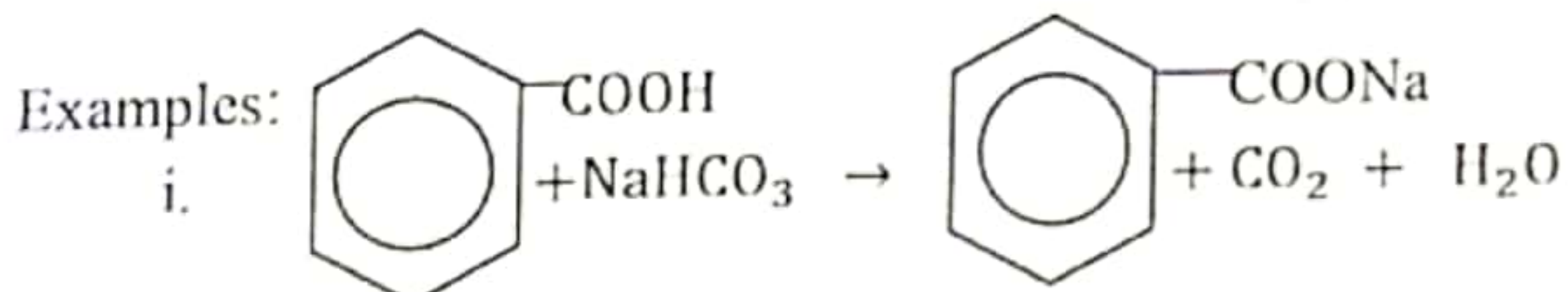
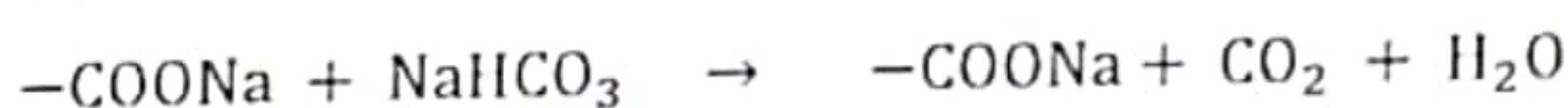
CHEMICAL REACTIONS OF CARBOXYLIC ACIDS

Reactions which involve $-COOH$ (carboxylic group)

a) Reaction with sodium bicarbonate (sodium hydrogencarbonate)

Carboxylic acid reacts with sodium bicarbonate to give sodium carboxylate and bubble of CO_2 are formed.

Generally;

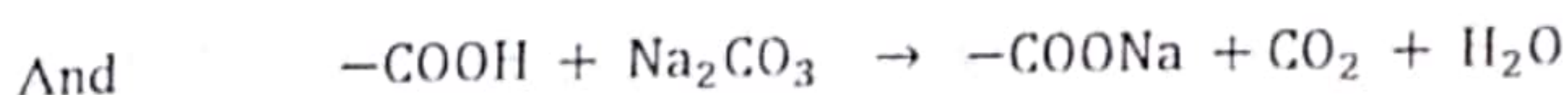
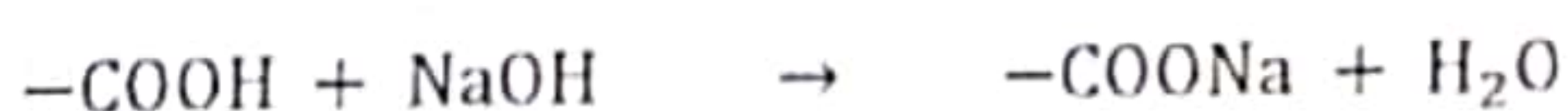


The reaction shows one of the differences between carboxylic acid on one side and alcohol and phenol on another side as alcohol and phenol do not react with $NaHCO_3$.

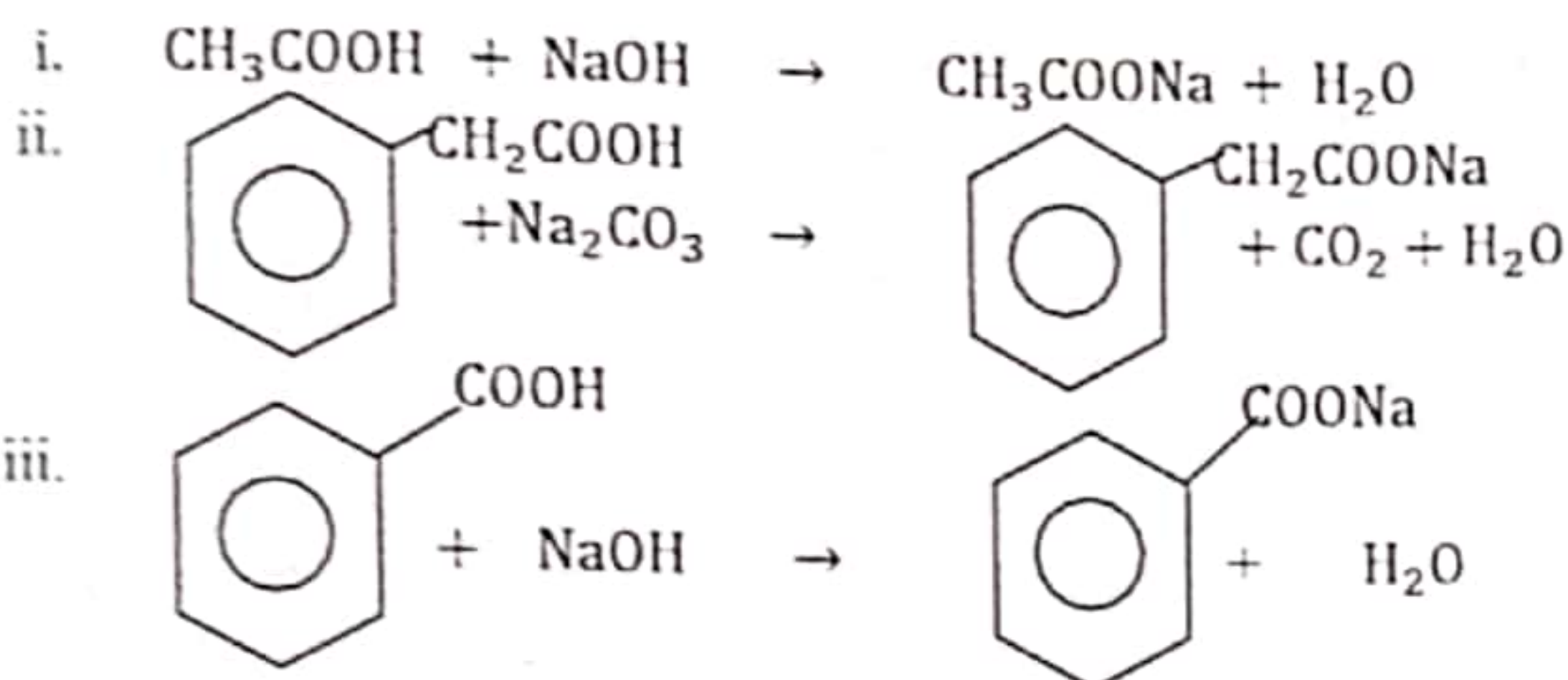
b) Reaction with alkali

Under this heading carboxylic acid reacts with alkali like $NaOH$ and Na_2CO_3 to form carboxylic salt.

Generally;



Examples:



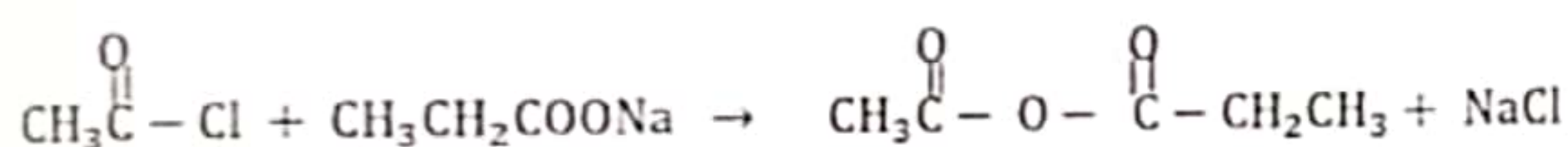
Phenol react with NaOH in the same way so the reaction give one of the similarities between carboxylic and phenol.

– However phenol is not strong acid enough to react with Na_2CO_3 and this gives another difference between phenol and carboxylic acid.

The reader should understand that:

The sodium carboxylate formed in the above reaction may react with acyl chloride like ethanoyl chloride to give an acid anhydride.

For example;



So in other words, carboxylic acid reacts with acyl (or acid) chloride under presence of NaOH to give an acid anhydride.

c) Reaction with strong metals

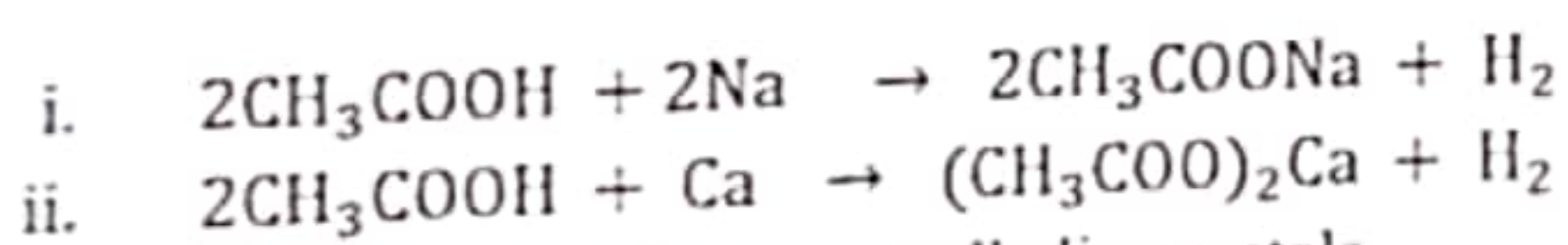
Carboxylic acid reacts with strong metal to give carboxylic salt and hydrogen gas is evolved.

Generally;



Where M is strong metal

Examples:



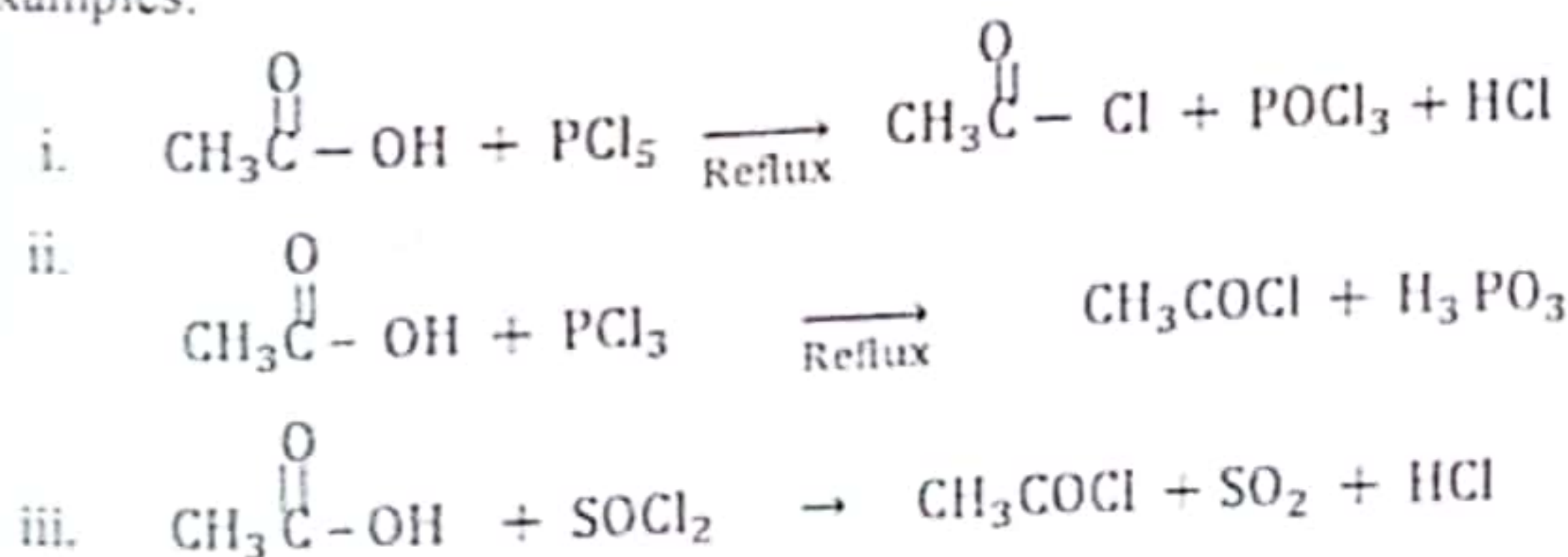
Alcohol and phenol also reacts with strong alkaline metals.

Reactions which replace OH from carboxic group ($-\text{COOH}$)

a) Halogenation

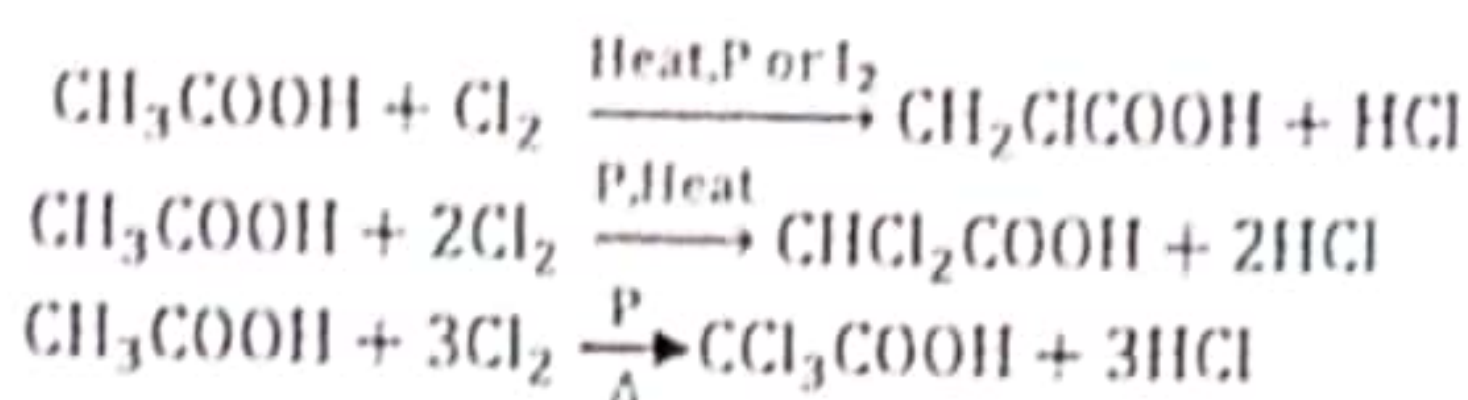
Carboxylic acid reacts with halogenating agent like PX_5 , PX_3 and SOX_2 to form acyl halide (acyl compounds).

Examples:



But if chlorine is bubbled into hot ethanoic acid in the presence of an iodine or phosphorous catalyst substitution reaction taken place at α carbon

For example;



Bromine substitute very slowly and iodine has almost no effect due to their little reactivity compared to chlorine.

b) Reaction with alcohol (Ester formation)

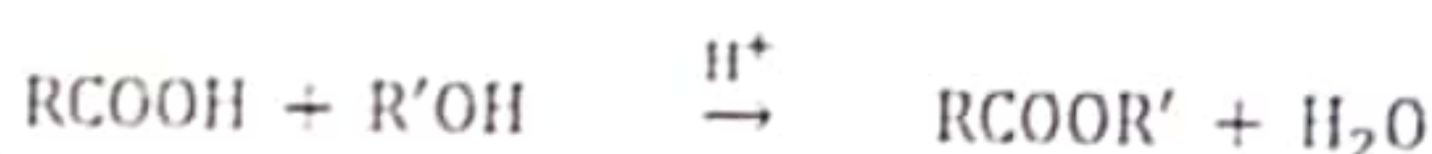
Carboxylic acid reacts with alcohol in presence of acidic medium like sulphuric acid to form ester. This reaction is known as **esterification**.

Understand this!

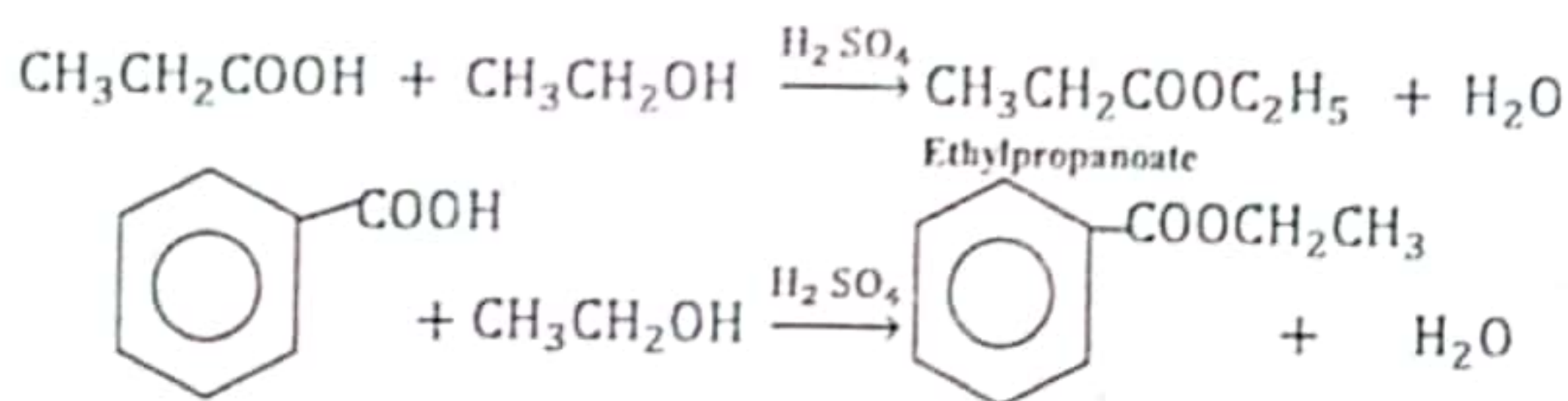
Although other acids like concentrated hydrochloric acid may catalyse the reaction, concentrated sulphuric acid is more preferable, why?

- This is because the concentrated sulphuric acid is good dehydrating agent, not only catalyse reaction like other acids but also remove water from the reversible acids reaction favouring more forward reaction
 - So the concentrated sulphuric acid has two functions in the esterification;
 - **It acts as catalyst thus enabling ester to be produced rate.** This is common function for any acid in this reaction.
 - **It acts as dehydrating agent thus shifting position of the equilibrium to the ester acid** (by removing water formed at the ester side) and hence **percentage yield of the ester become high.**
- This is the extra function of H_2SO_4 which is not exhibited by other acids like HCl .

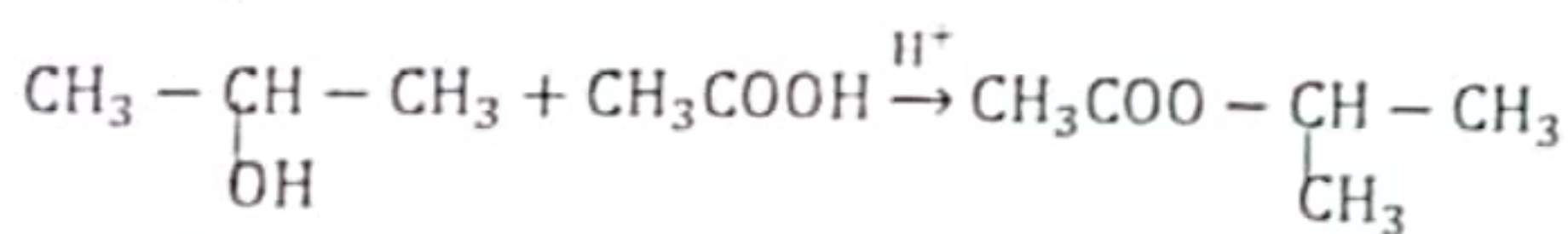
Generally;



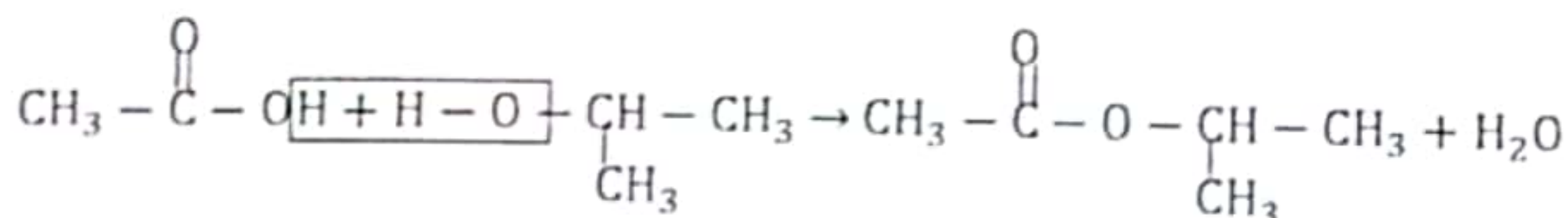
Examples:



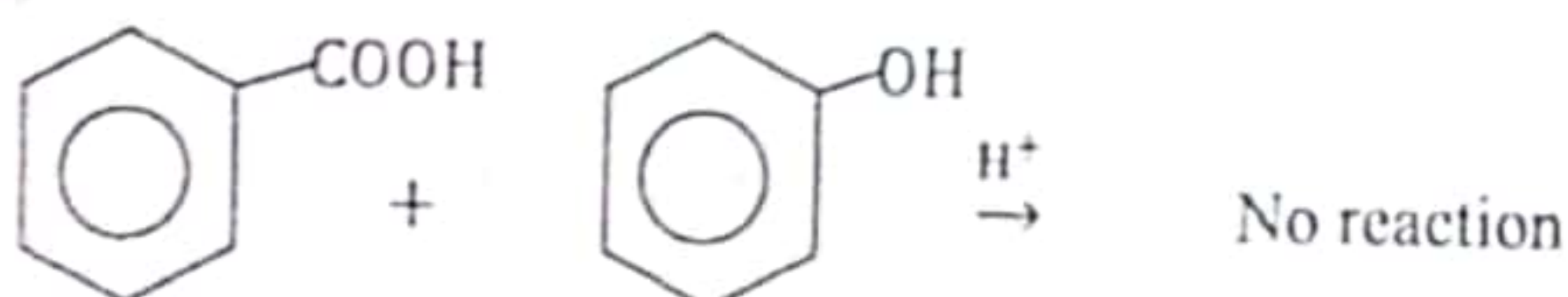
Similarly;

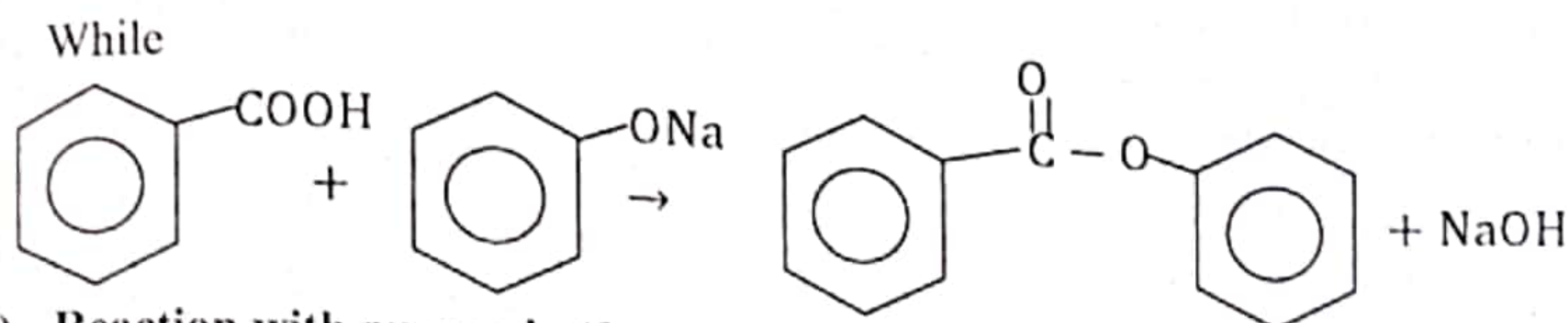


Memorising:



But;

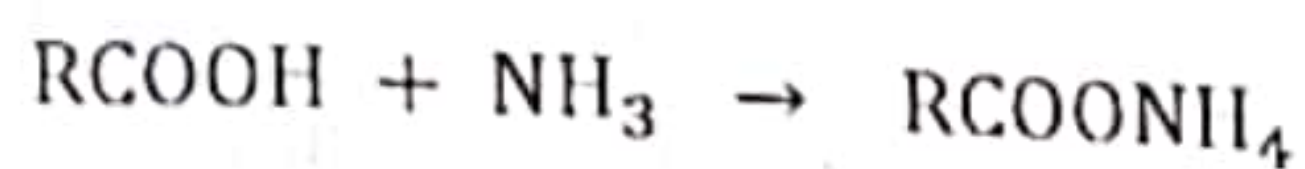




c) **Reaction with ammonia (formation of amide)**

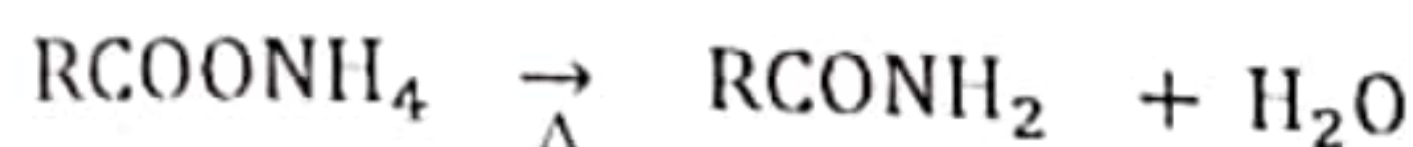
Carboxylic acid when heated with dry ammonia tends to form amide.

Generally;

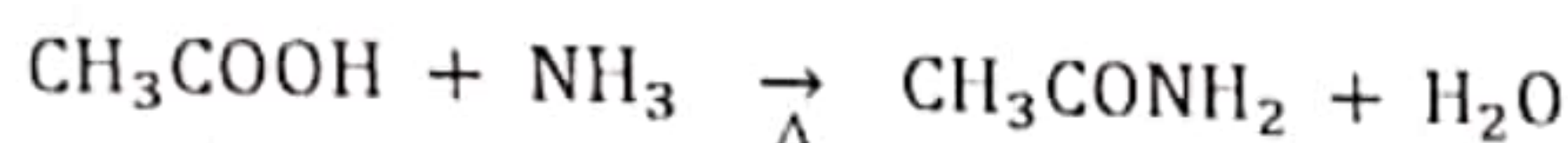


When the product is heated, amide is formed

i.e

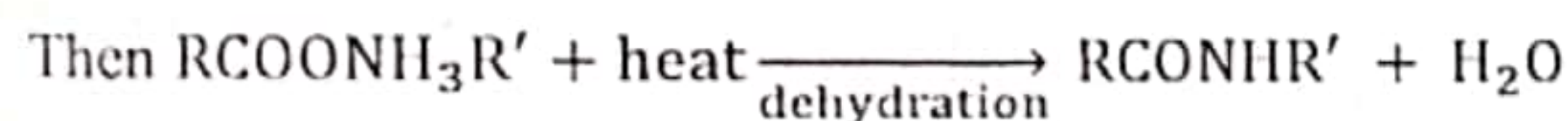
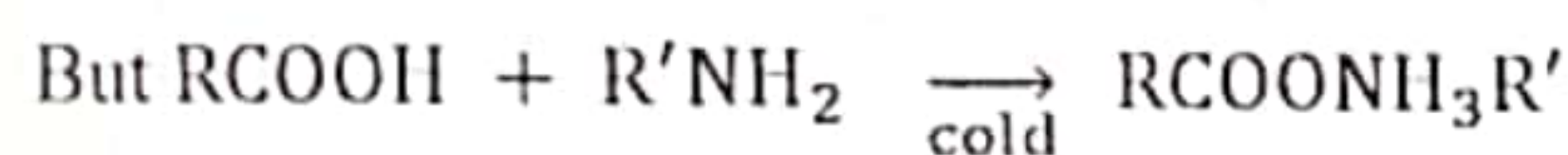
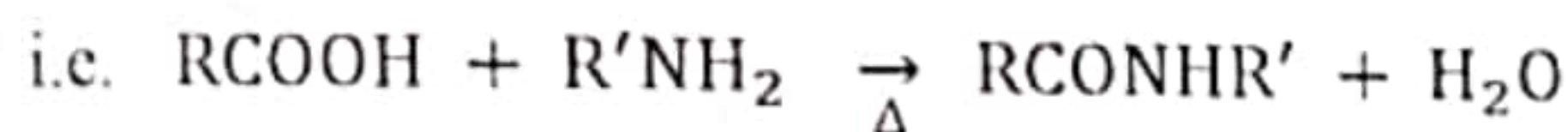


Example,



d) **Reaction with amine**

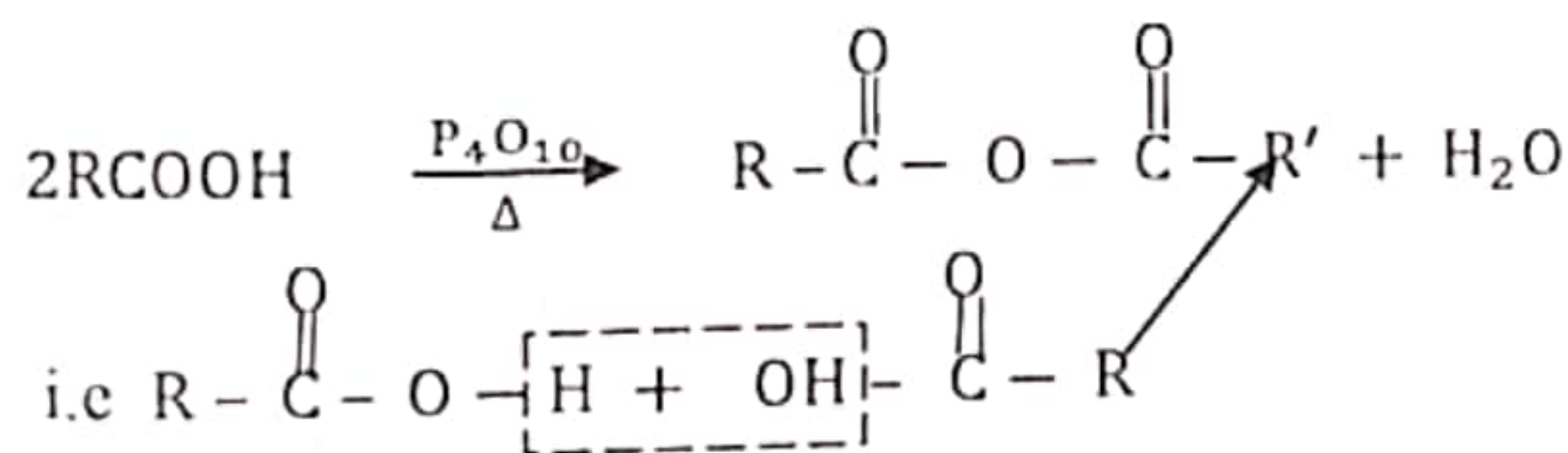
Carboxylic acid also reacts with amine to give N-substituted amide.



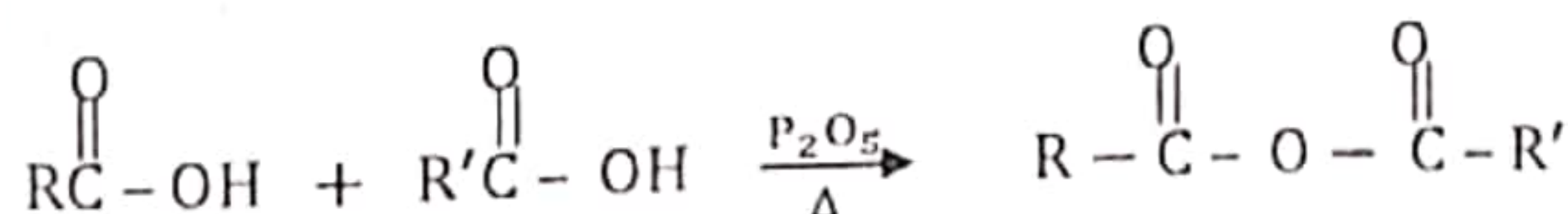
Dehydration of carboxylic acids

Carboxylic acids give an acid anhydride on heating with phosphorous (v) oxide which is good dehydrating agent.

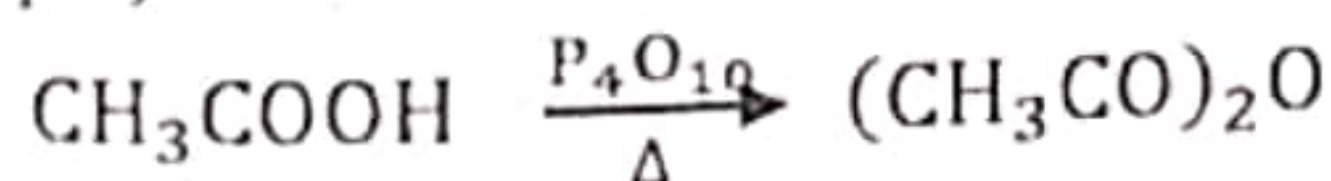
Generally;



Similarly;

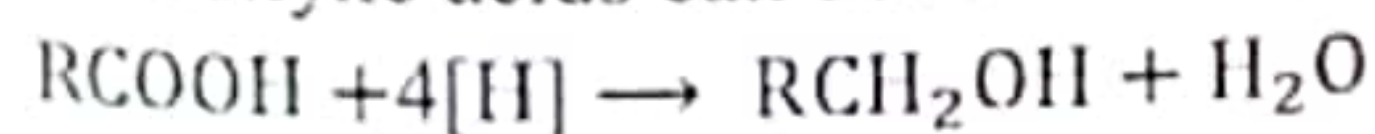


Example,



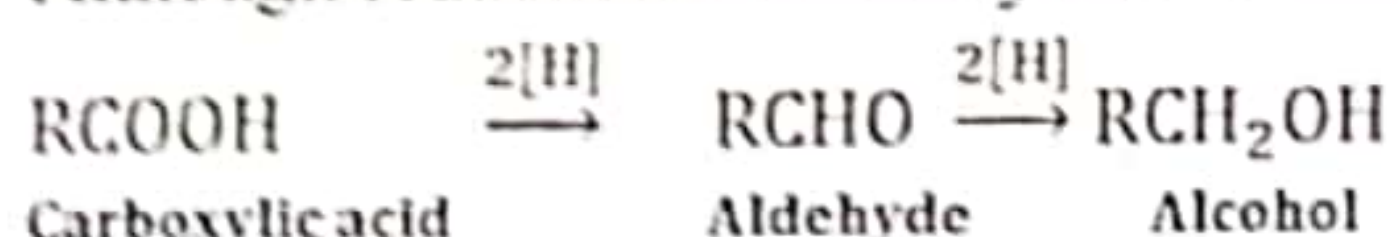
Reduction

Carboxylic acids can be reduced by strong reducing agent like LiAlH_4 to give alcohol.



Be Careful!

Although reduction of carboxylic acid takes place in step as shown below;



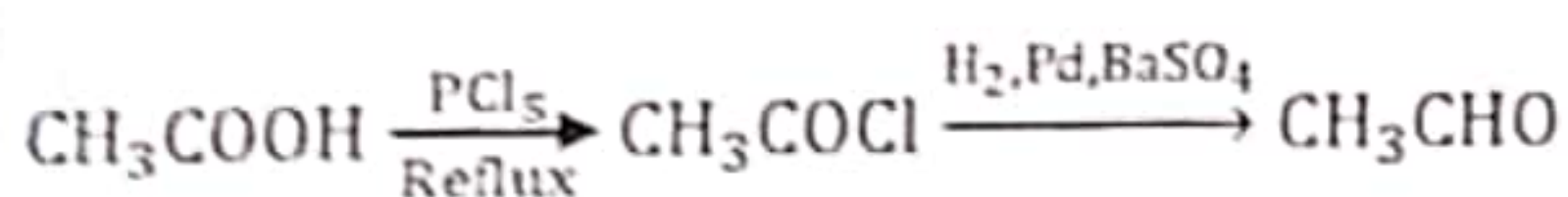
Partial reduction of carboxylic acids directly to aldehyde is not possible

- This is because weak reducing agent like NaBH_4 does not reduce carboxylic acid. To reduce carboxylic acid, strong reducing agents are needed which tend to reduce carboxylic acid to alcohol
- To convert carboxylic acid to aldehyde at least two steps are needed via certain carboxylic acid derivatives.

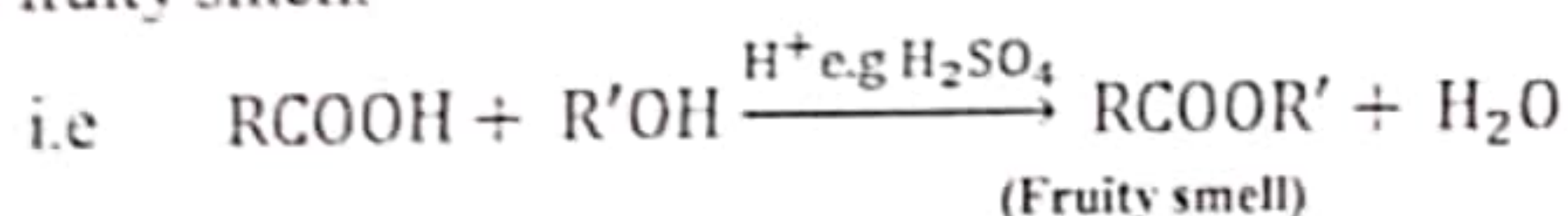
To insist! NaBH_4 is not powerful reducing agent enough to reduce carboxylic acid.

Example

Show how would you convert CH_3COOH into CH_3CHO

Solution**CHEMICAL TESTS OF CARBOXYLIC ACIDS****a) Reaction with alcohol**

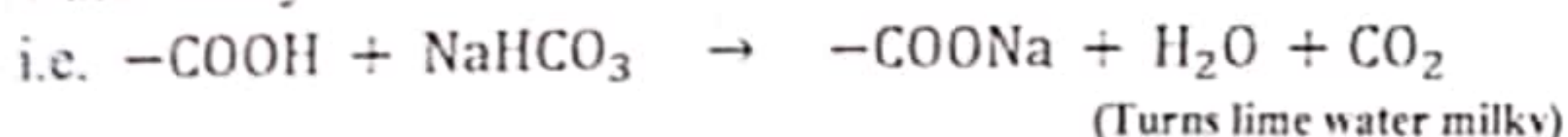
Carboxylic acids react with alcohol in presence of acidic medium to form ester which is recognised by its fruity smell.



This reaction is very important in distinguishing carboxylic acid from phenol as phenol does not react with alcohol verifying that carboxylic acid is more acidic than phenol.

b) Reaction with sodium bicarbonate

Carboxylic acid reacts with NaHCO_3 to give effervescence of carbon dioxide gas which turns lime water milky.



The reaction gives another difference between carboxylic acid and phenol as phenol does not give effervescence with NaHCO_3 verifying that carboxylic acid is more acidic than phenol.

c) Reaction with FeCl_3 (Ferric chloride test)

Iron (III) chloride reacts with carboxylic acid to give Iron (III) carboxylate which appear in buff colouration.



The reaction is very important in distinguishing between alcohol, phenol and carboxylic acid.

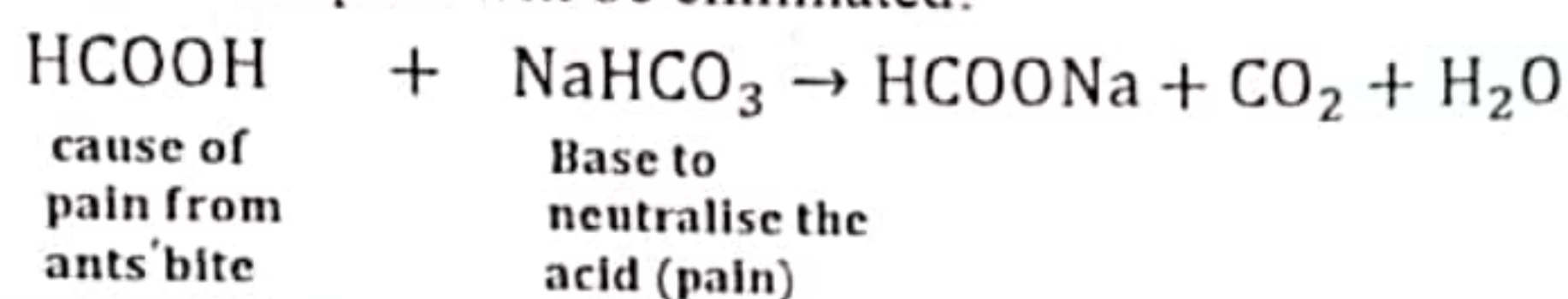
- Alcohol give no change indicating that there is no reaction between alcohol and FeCl_3
- Phenol gives purple /violet coloured compound.
- Carboxylic acid give buff coloured compound.

Uses of some common carboxylic acids

(i) Methanoic acid

Methanoic acid (common name: formic acid) is an acid found in some ants' sting (the name formic acid comes from the Latin name *formica* which means **ant**).

- The pain associated with ant's bite is due to the formic acid released from the ant's sting.
- So if one rubs a base like sodium bicarbonate on the afflicted surface quickly, it will neutralise the formic acid and some of the pain will be eliminated!



Formic acid is commonly used as **preservative and antibacterial agent**

- It also used in rubber, textile, dyeing, leather and electroplating industries.

(ii) Ethanoic acid

Ethanoic acid (common name: acetic acid) is the main acid in vinegar (the term 'acetic' comes from Latin word "*acetabulum*" which is a shallow cup used in Roman times for vinegar)

- Like methanoic acid ethanoic acid is colourless liquid with pungent odour

Ethanoic acid is used in the following ways:

- | | |
|---|---|
| ▪ In the manufacture of rayon (textile fibre) | ▪ As a coagulant in the manufacture of rubber |
| ▪ In the manufacture of plastic | ▪ As a solvent |
| | ▪ In the food industry as vinegar |

(iii) Trichloroacetic acid (TCA)

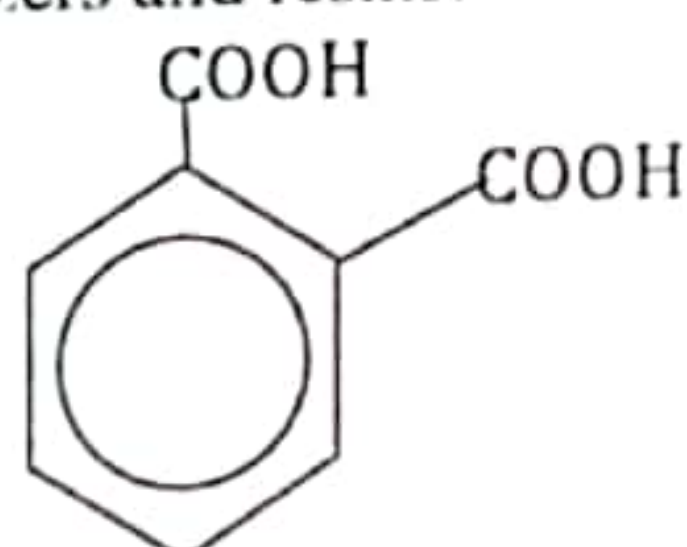
This (CCl_3COOH) is stronger acid than ethanoic acid.

- It is used to burn chemically warts and for facial peels.

(iv) Benzoic acid

Benzoic acid can be in various forms:

- In the form of esters, benzoic acid is used in perfume industry
- In the form of salt (like sodium benzoate), it used as food preservative
- 1,2 - benzene dicarboxylic acid (common name: phthalic acid or ortho-phthalic acid) is used in the manufacture of plasticizers and resins.



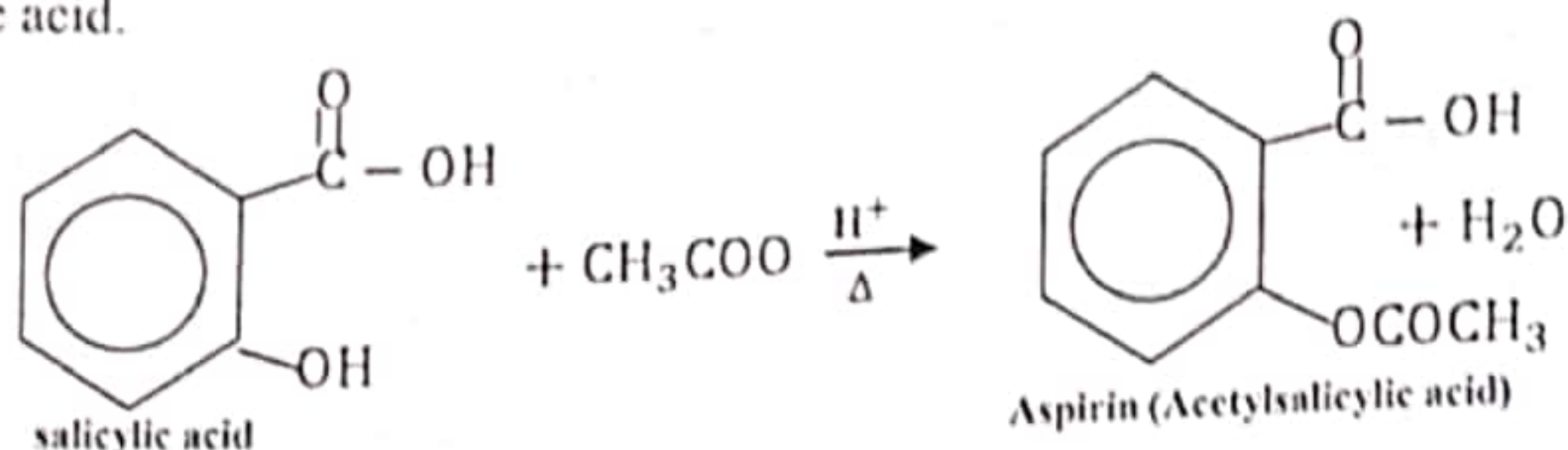
Common name: phthalic acid or ortho-phthalic acid
IUPAC name: 1,2 - benzene dicarboxylic acid

- 1,4 - benzene dicarboxylic acid (Common name: terephthalic acid) is the raw material (monomer) for manufacture of polyester.



Common name: terephthalic acid or para-phthalic acid
IUPAC name: 1,4 - benzene dicarboxylic acid

- Benzoic acid in the form of aspirin is a drug used to relieve pain and inflammation. It also reduces fever and is taken regularly by those at risk from heart attacks. Aspirin is an ester of salicylic acid and ethanoic acid.



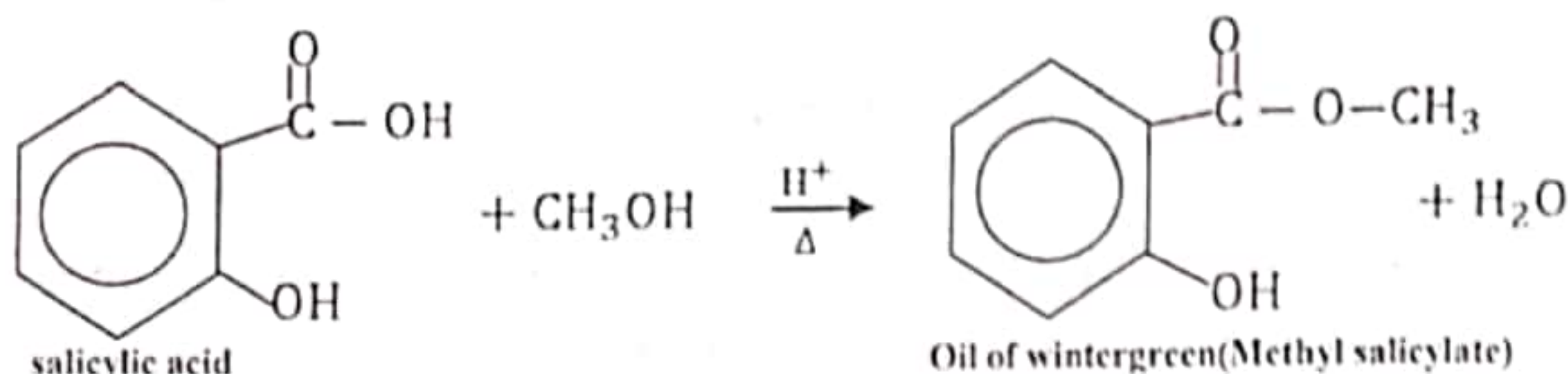
The reader should understand that:

Like aspirin, salicylic can reduce fever and relieve pain and inflammation; however it is not commonly used as commercial drug, why?

Reason:

Salicylic acid is stronger acid than aspirin and therefore it causes irritation of the mucous membrane (tissue which secretes mucus) in the mouth, throat and stomach, and can cause painful ulcers and stomach bleeding.

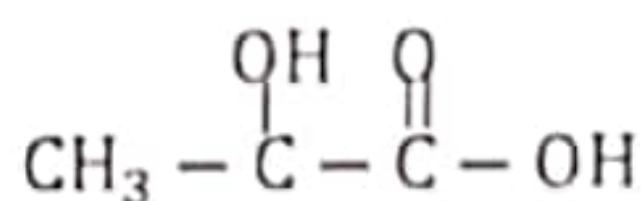
- Oil of wintergreen which is an ester of salicylic acid (derivative of benzoic acid) and methanol is used to soothe sore muscles.



(v) Lactic acid

Lactic acid (IUPAC name: 2-hydroxypropanoic acid) is produced (by *Lactobacillus acidophilus*) in yogurt and by muscle cells during anaerobic exercise.

- It is mainly used in a variety of skin care products.



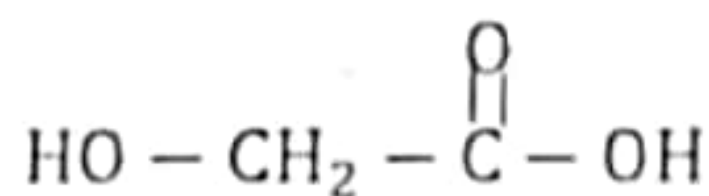
Common name: lactic acid

IUPAC name: 2-hydroxypropanoic acid

(vi) Glycolic acid

Glycolic acid (IUPAC name: 2-hydroxyethanoic acid) is a solid which is commonly used in a variety of skin care products for removing wrinkles and making skin look younger.

- It works the same way as phenol and trichloroacetic acid, dissolving away the outer layer of skin.



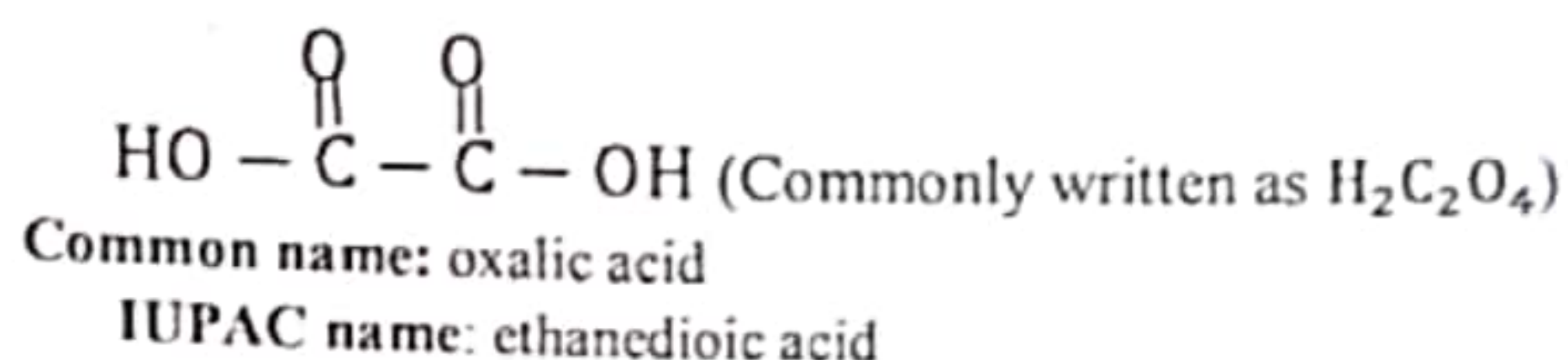
Common name: Glycolic acid

IUPAC name: 2-hydroxyethanoic acid

(vii) Oxalic acid

Oxalic acid (IUPAC name: ethanedioic acid) may be naturally found in spinach and some other plants.

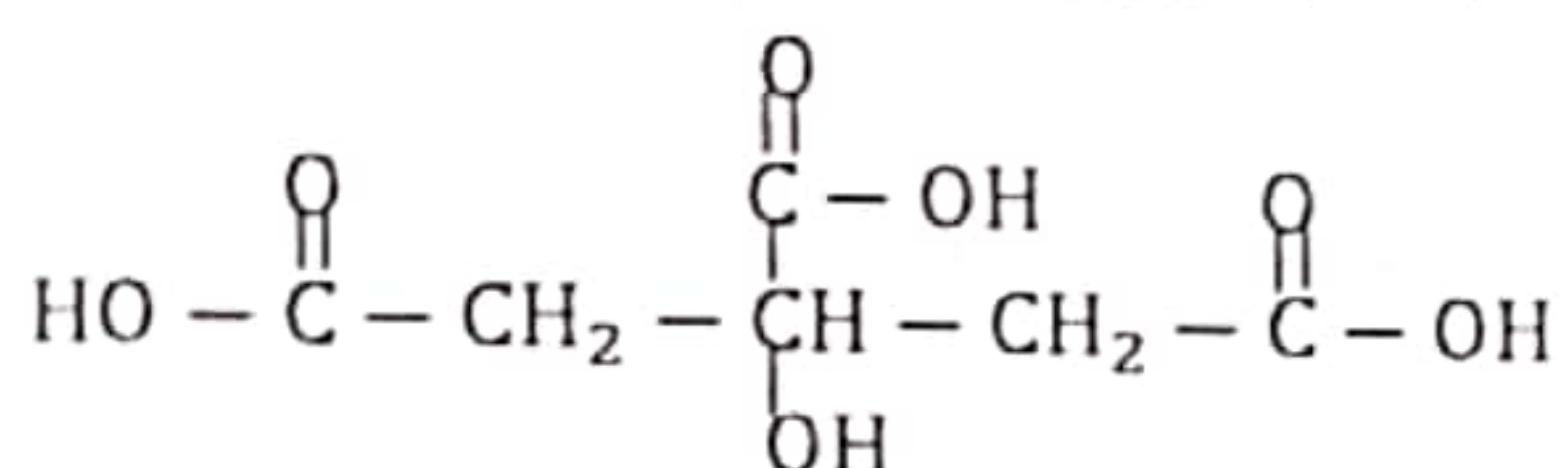
- It is common available in hardware stores for cleaning off iron stains.



(viii) **Citric acid**

Citric acid is found in some fruits, especially lemons and orange. It also found in other citrus fruits like lime and grape fruits.

- It is used as natural preservative for foods and drinks.
- It also used in food industry to add sour test to food drinks.



Common name: citric acid
IUPAC name: 3 - carboxy - 3 - hydroxypentanedioic acid

HAZARDS OF CARBOXYLIC ACIDS

Generally toxicity of monocarboxylic acid varies from moderate to low and decreases as the length of carbon chain increases. For dicarboxylic acids, their toxicities vary from moderate to high and decreases with an increase in carbon chain length. Aromatic carboxylic acids have generally low toxicity.

- Below are hazards of some common carboxylic acids

(i) **Methanoic acid**

At higher concentration, formic acid is corrosive and produces dangerous fumes.

- It produces burns on the skin and injures the eyes and mucous membranes in the mouth, throat and respiratory system.
- Inhaling concentrated formic acid makes it hard for person to breath.
- Swallowing the concentrated formic acid causes severe ulcers to appear in digestive tract as well as pain and nausea.
- Prolonged exposure to formic acid may produce liver or kidney damage.

(ii) **Ethanoic acid**

Exposure to concentrated ethanoic acid may lead to problems on eyes, skin, respiratory system and digestive tract.

- On contact with the concentrated acid may make the skin to appear red and may lead to serious skin burn.
- Contact with eyes may lead to
 - Pain
 - Redness
 - Blurred vision
 - Sever deep burns
- Inhalation of concentrated acetic acid vapour may lead to
 - Sore throat
 - Cough
 - Shortness of breath
- Indigestion (swallowing) may lead to:
 - Abdominal pain
 - Burning sensation
 - Diarrhea
 - Sore throat
 - Vomiting

(iii) **Benzoic acid**

Inhalation of benzoic acid vapour may lead to:

- Cough

- Irritant

Eyes contact may lead to

- Redness
- Irritant

- Pain

Indigestion of the acid may lead to:

- Adominal pain
- Nausea

- Vomiting

(iv) **Oxalic acid**

Inhalation may lead to:

- Cough
- Shortness of breath

- Sore throat

Skin contact may be lead to:

- Absorption of the acid in the skin
- Dry skin
- Redness

- Skin burns
- Pain
- Blusters

Eyes contact may lead to:

- Redness
- Pain

- Severe deep burns

Indigestion may lead to:

- Abdominal cramps
- Sore throat
- Vomiting

- Weakness
- Convulsions

PRACTICE EXERCISE 20

Problem 1

Give structures of the following organic compounds:

- i. Formic acid
- ii. Acetic acid
- iii. Oxalic acid
- iv. Citric acid
- v. Lactic acid

Problem 2

Write down chemical equation to show preparation of ethanoic acid by:

- i. Oxidation of alcohol
- ii. Hydrolysis
- iii. Hydrolysis of nitrile
- iv. Hydrolysis of ester
- v. Oxidation of ethanol
- vi. Oxidation of but-2-ene

Problem 3

Complete and balance the following reactions:

- i. $\text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{H}^+}$
- ii. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COCl} \xrightarrow{\text{NaOH}}$
- iii. $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_5}$
- iv. $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow$
- v. $\text{CH}_3\text{COOH} + \text{NaBH}_4 \rightarrow$

Problem 4

Mention at least one use of each of the following in daily life.

- i. Methanoic acid
- ii. Ethanoic acid
- iii. TCA
- iv. Benzoic acid
- v. Lactic acid
- vi. Oxalic acid
- vii. Citric acid
- viii. Glycolic acid

Problem 5

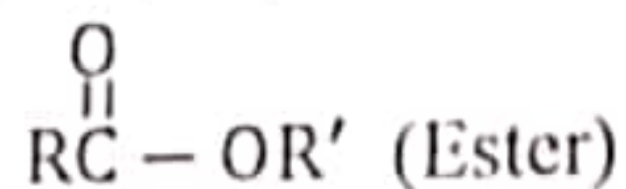
Give at least two hazards of each of the following.

- i. Methanoic acid
- ii. Ethanoic acid
- iii. Benzoic acid
- iv. Ethanedioic acid

Chapter 21 ESTER

INTRODUCTION

Ester is formed when OH in carboxylic acid is replaced by an alkoxide group.



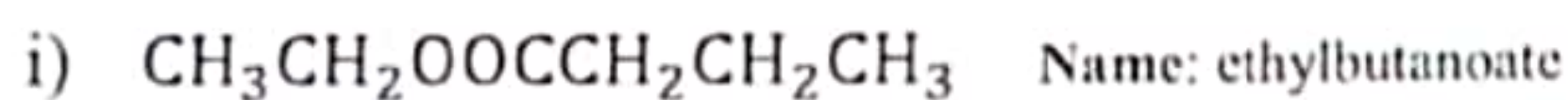
Esters have general molecular formula of $\text{C}_n\text{H}_{2n}\text{O}_2$

- Thus carboxylic acids and esters are function isomers.
- For example $\text{CH}_3\text{CH}_2\text{COOH}$ is function isomer of $\text{CH}_3\text{COOCH}_3$

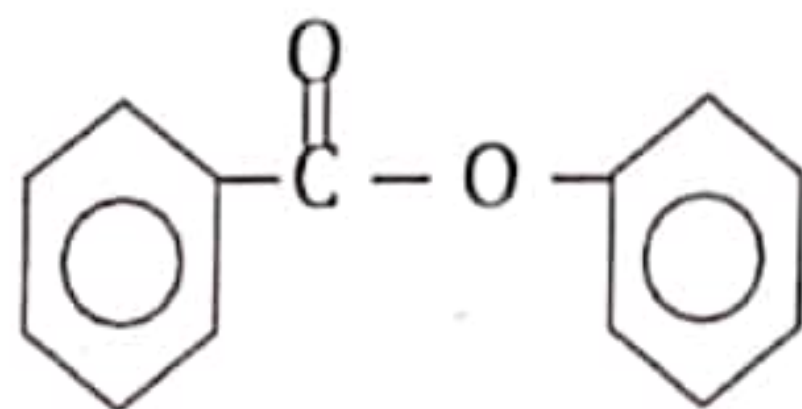
Nomenclature

Esters are named as alkyl alkanoate where alkyl is the name of alkyl group in alkoxide which replaces OH.

Examples:



ii)

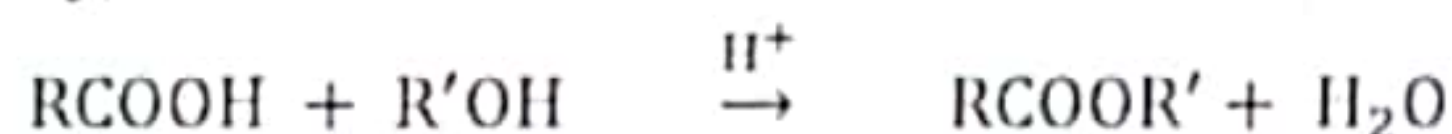


Name: phenylbenzoate

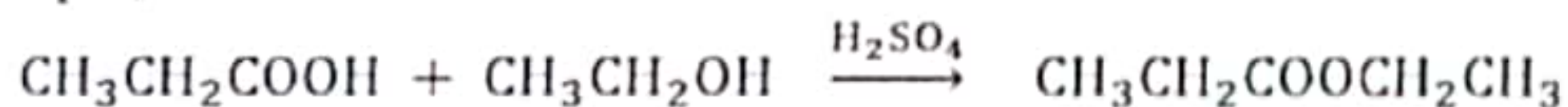
PREPARATIONS OF ESTER

a) Reaction between carboxylic acid and alcohol under acidic medium

Generally;



Example,

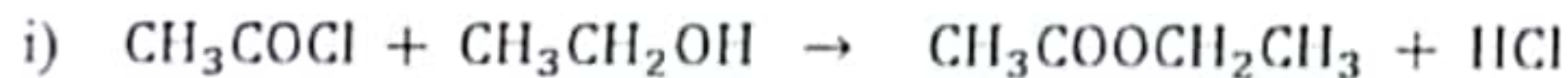


b) Reaction between acyl chloride and alcohol (or phenol)

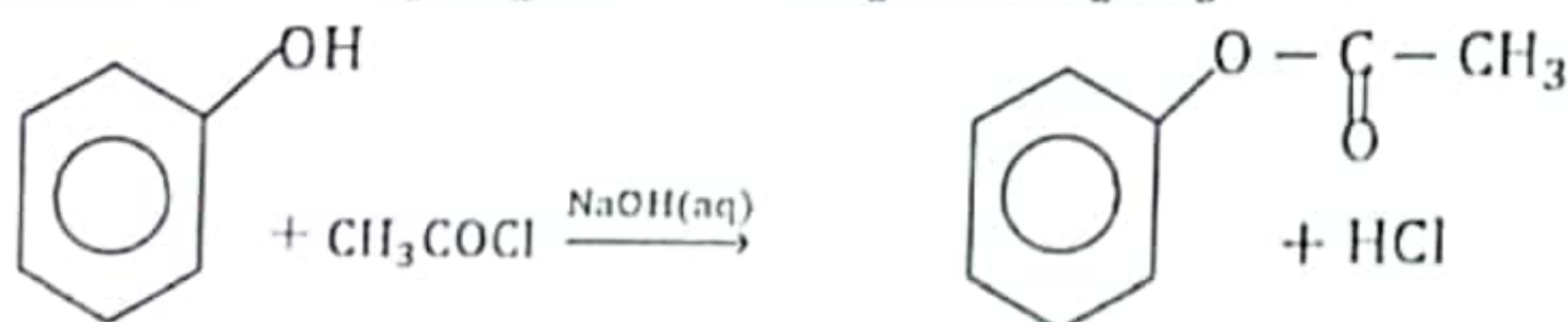
Generally;



Examples:

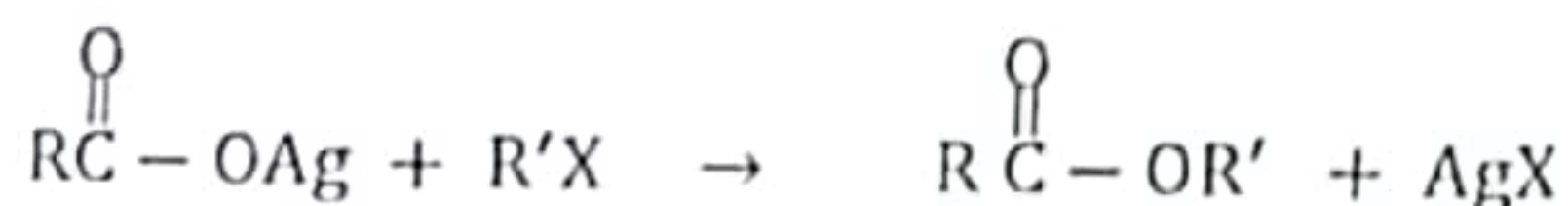


ii)

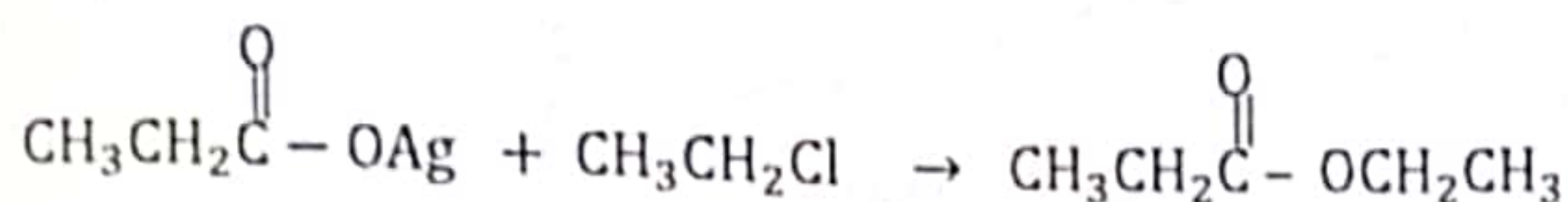


c) Reaction between silver salt or carboxylic acid and haloalkane

Generally;



Example,

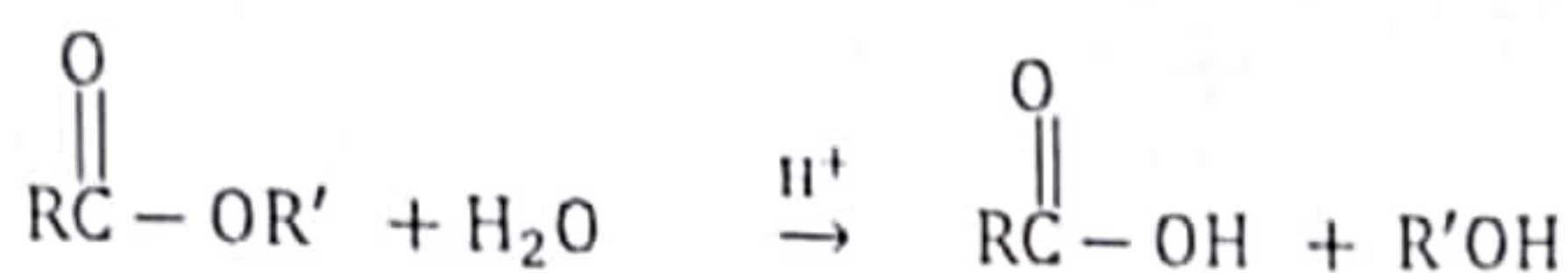


CHEMICAL REACTIONS OF ESTER

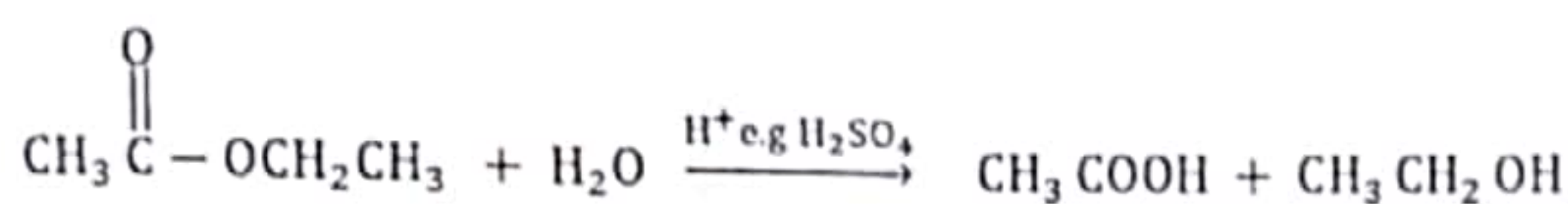
Hydrolysis

Ester undergoes hydrolysis in presence of acidic medium to form carboxylic acid and alcohol.

Generally;

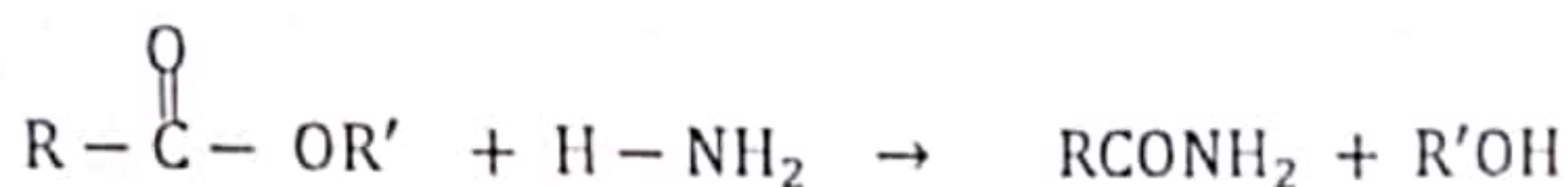


Example,

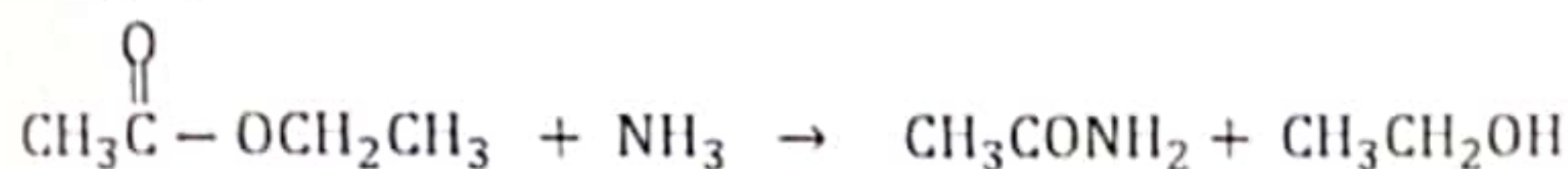


Reaction with ammonia

Generally;

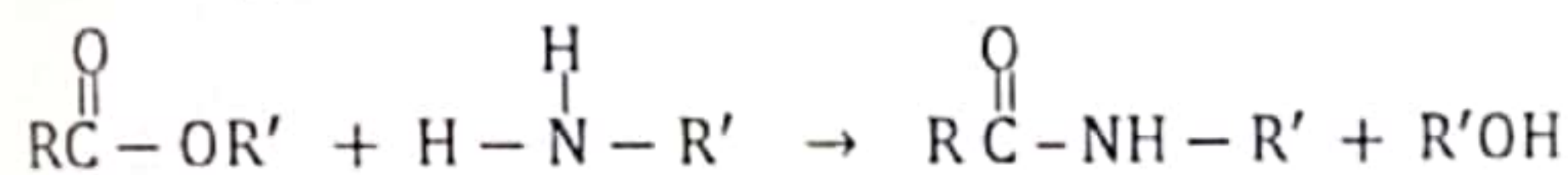


Example,

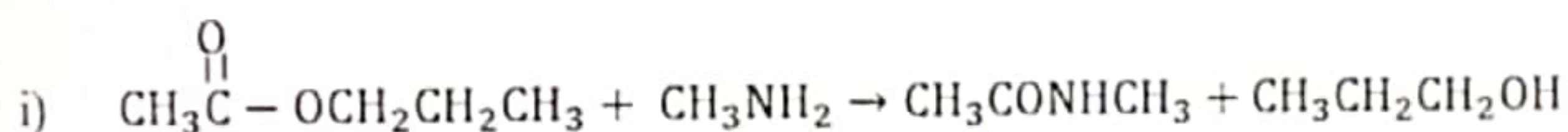


Reaction with amine

Generally;



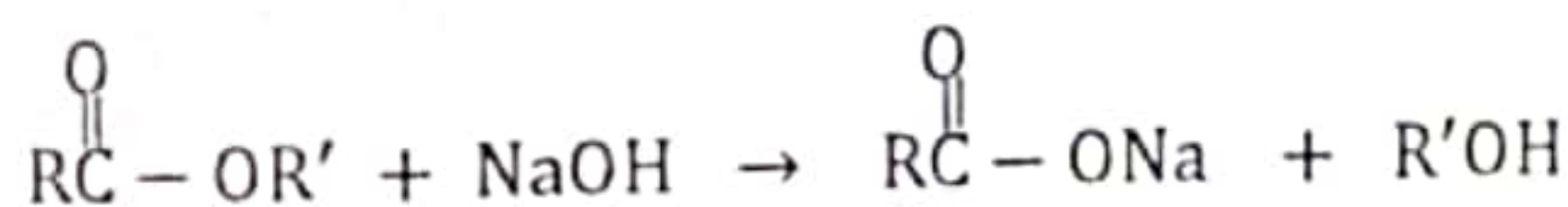
Example;



Partial hydrolysis of ester (Reaction with alkaline solution)

Alkaline hydrolysis of ester is known as saponification.

Generally;



Example

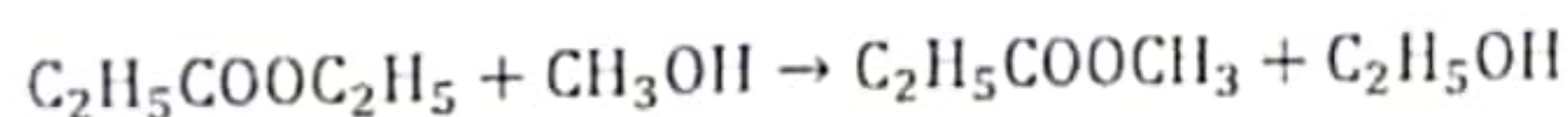


Transesterification

Ester reacts with alcohol to form another ester

i.e $\text{RCOOR}' + \text{R}''\text{OH} \rightarrow \text{RCOOR}'' + \text{R}'\text{OH}$

Example;



USES OF ESTERS

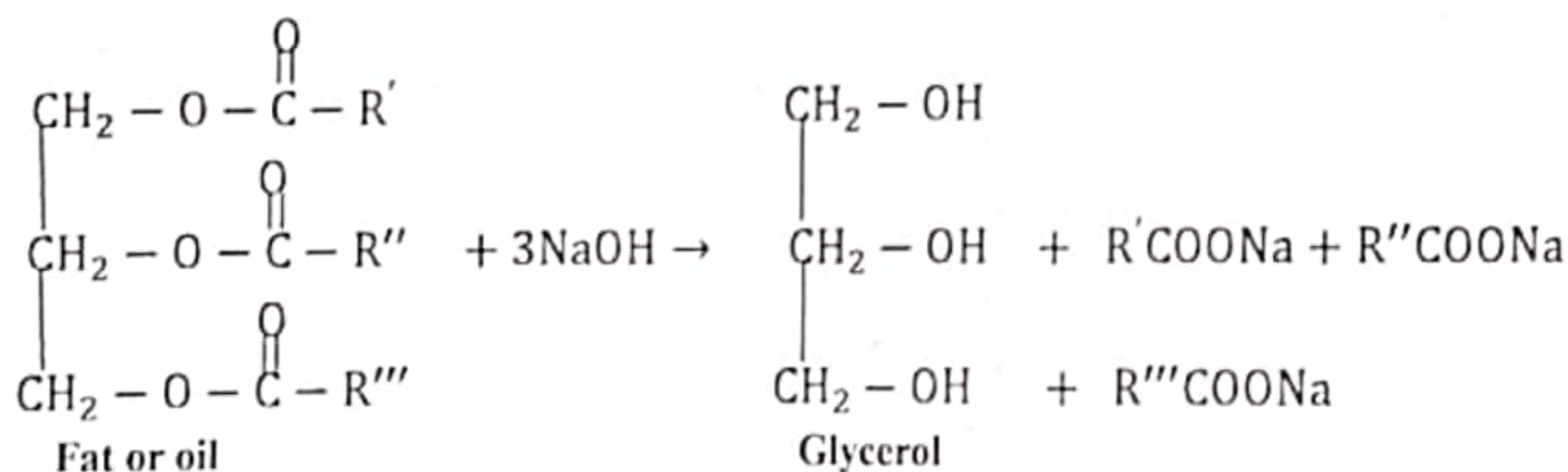
Applications of esters include:

- (i) Making of soap
- (ii) As solvent

i) In making of a soap

Soaps are chemical salts of long chain **fatty acid** (carboxylic acids with terminal carboxylic group with aliphatic chain).

- Are made by the basic (alkaline) hydrolysis of the ester (fats and oil) by the reaction which is known as **saponification**.
- If the base (alkali) is sodium hydroxide, then the soap is sodium salt
- For example if the alkali used is NaOH, the equation of saponification process (reaction) is as follows.



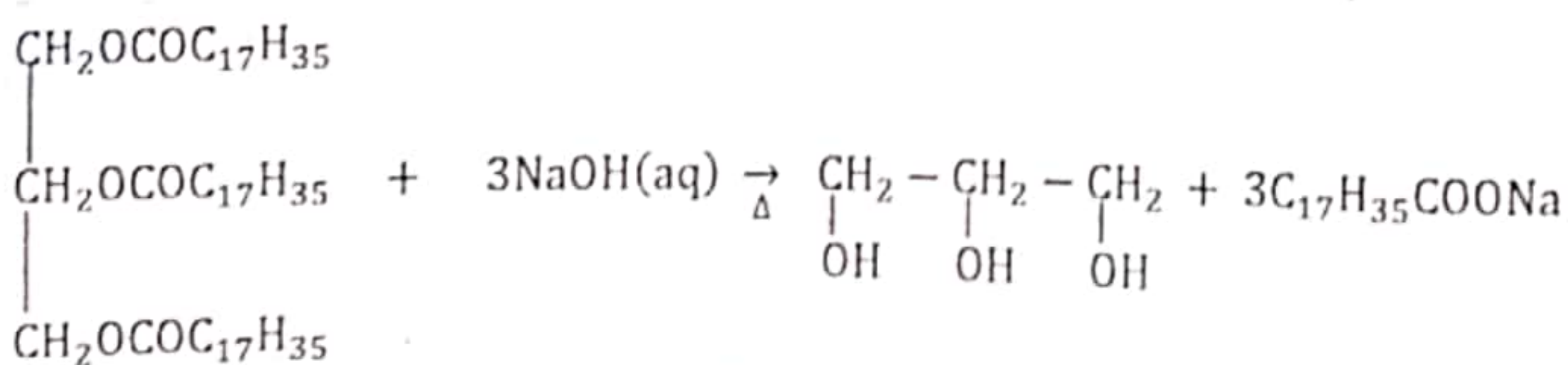
Where R' , R'' and R''' are alkyl groups with more than 10 carbons. For example;

- $\text{C}_{15}\text{H}_{31}\text{COONa}$ (sodium palmitate)

This is the soap which is sodium salt of **palmitic acid** that is derived from **palm oil**

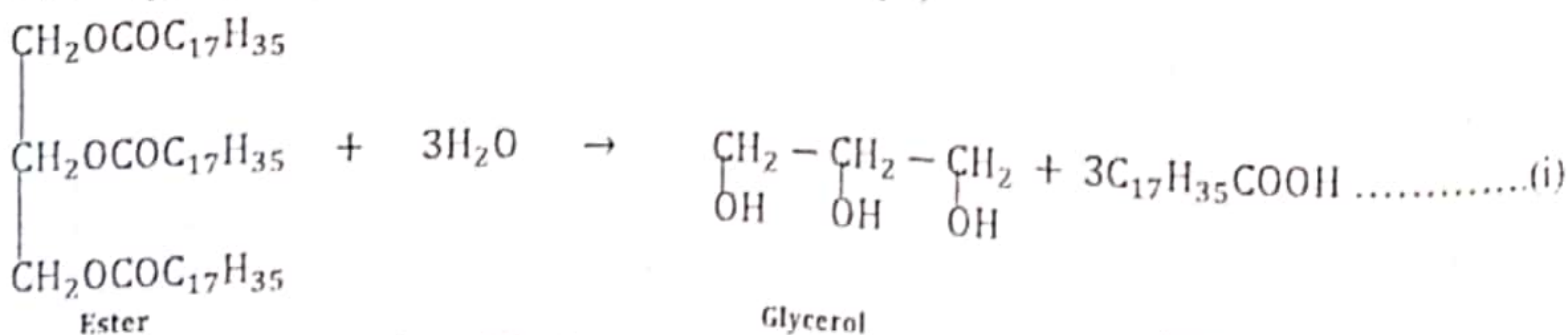
- $\text{C}_{17}\text{H}_{35}\text{COONa}$ (sodium stearate)
- $\text{C}_{11}\text{H}_{23}\text{COONa}$ (sodium laurate)

The most common soap is the sodium stearate which is formed as per equation;

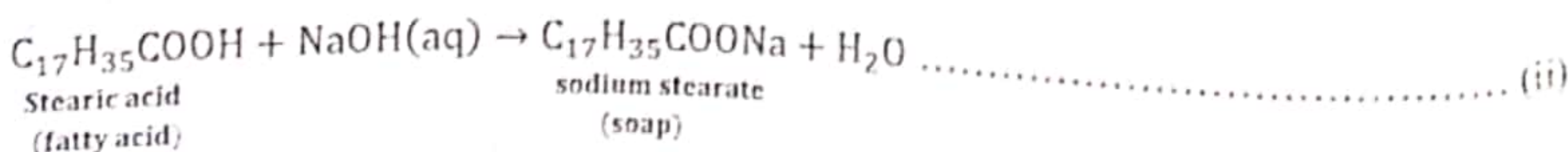


The reaction takes place in two steps as follows:

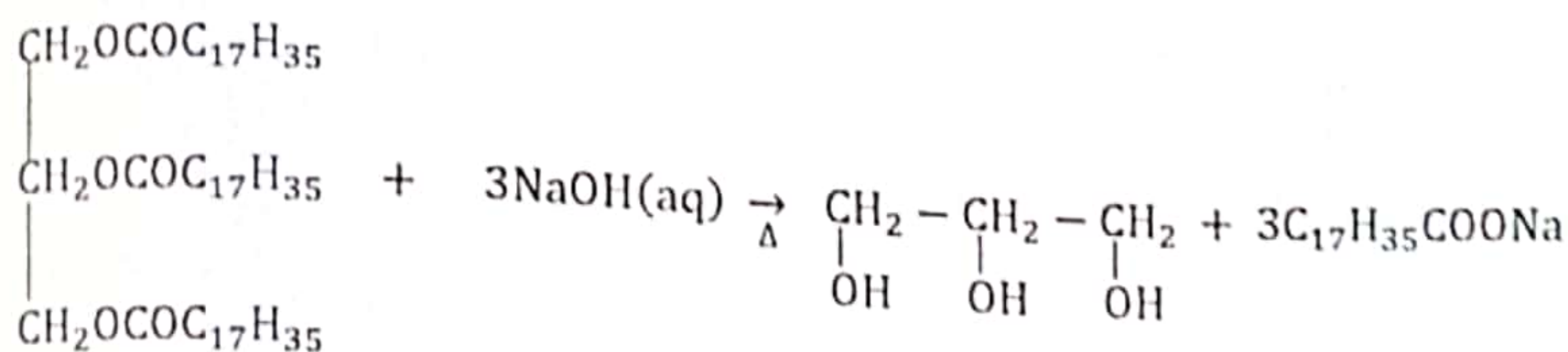
First step: Hydrolysis of ester (where NaOH act as catalyst)



Second step: Neutralisation of the fatty acid by NaOH



The overall reaction equation is obtained by taking (i) + 3(ii)



Ester

Glycerol

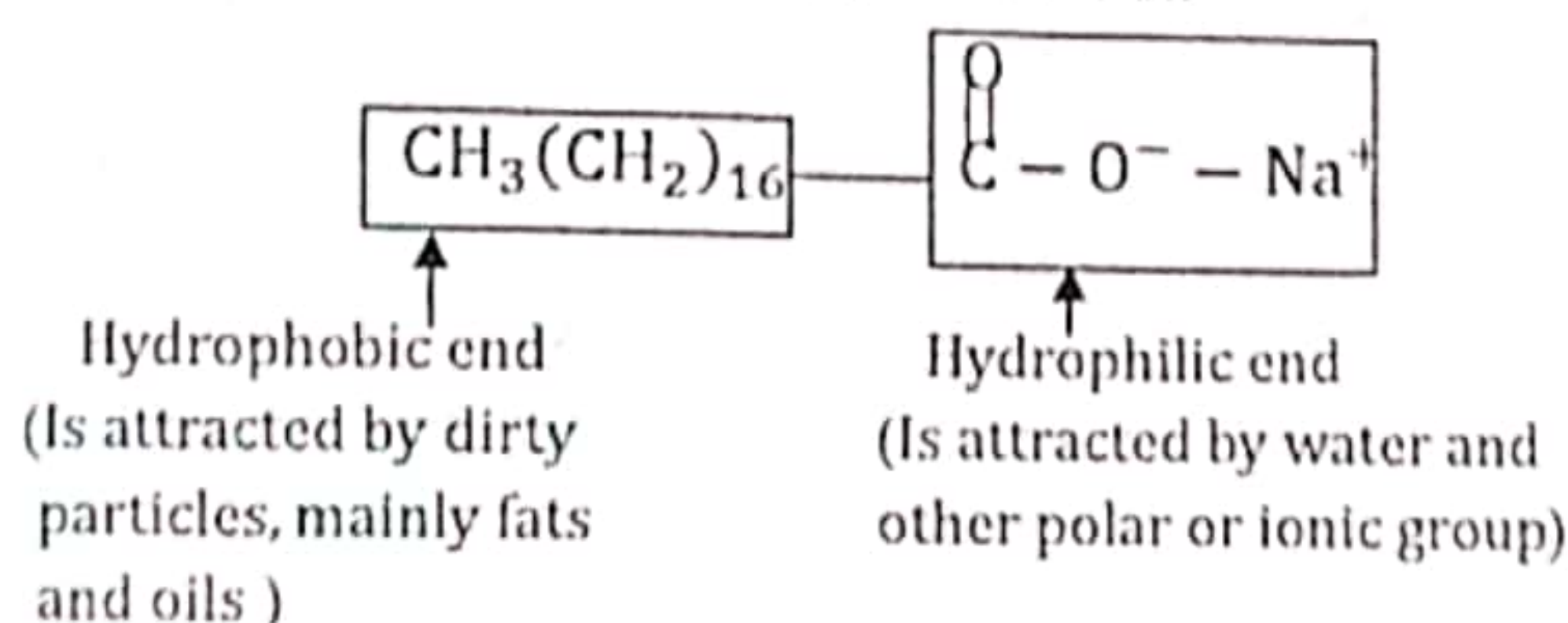
Soap

(Note: Glycerol is useful by-product of this reaction as it can be used to make pharmaceuticals and cosmetics).

How soap do cleansing action?

Soap molecules have polar end, which is the carboxylate group that attract (or is attracted by) water and other hydrophilic (water loving) groups.

- They also have non-polar end which is the long chain hydrocarbon (alkyl) group that attract (or is attracted by) oils and other hydrophobic (water hating) groups (dirtiness)-Remember “like dissolve like”
- Here is the sodium stearate for the illustration



Thus the same molecule is attracted to aqueous species and oil species and hence enabling them to mix.

- As result these oil species (dirtiness) will come off skin (or cooking utensils or any other substance to be cleaned) into water which contains soap and eventually on rinsing the dirty (oil species) will be carried away.

In just sentence to summarise cleansing action of soap!

Soap does cleansing action by helping oil species and water to mix together.

ii) As a solvent

Ester has no free OH groups (like their isomeric carboxylic acids) and therefore they tend to be insoluble in water.

- However they are very good solvents for non-polar organic compounds such as printing ink, polystyrene and nail vanish as well as being used in the pharmaceutical industry.

Other uses of ester

• As plasticizers

- Ester can be added to polymers make them less rigid and more flexible. (Plasticizer molecules weaken the intermolecular force between polymers chains).

• As food flavourings

- Ester has fruit smell and natural fruit flavour are mixtures of esters and carboxylic acids
- General artificial flavour contains many ingredients but esters always major components

For examples:

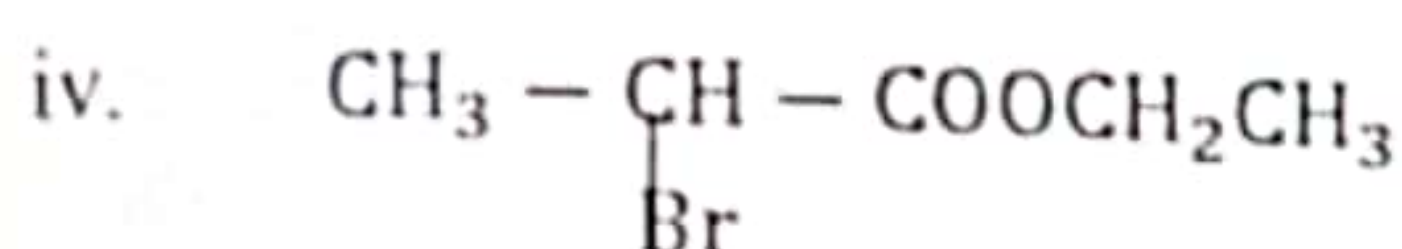
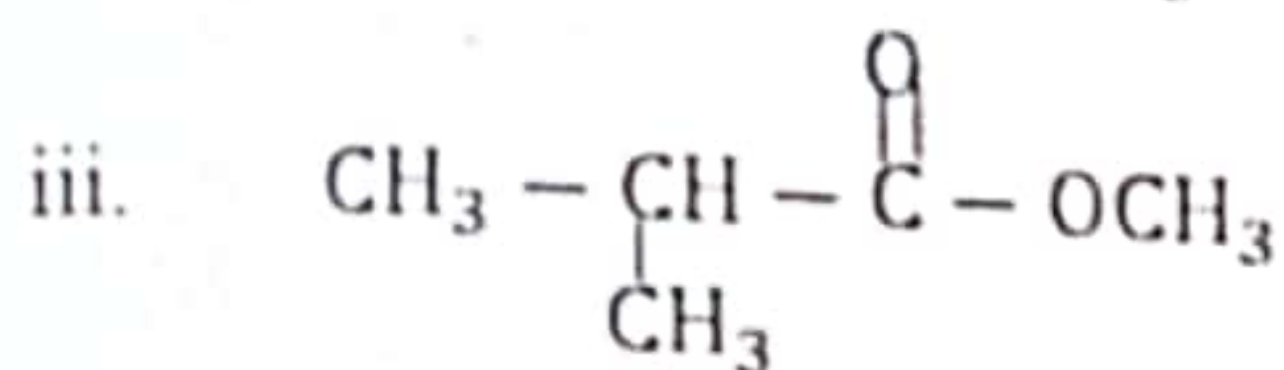
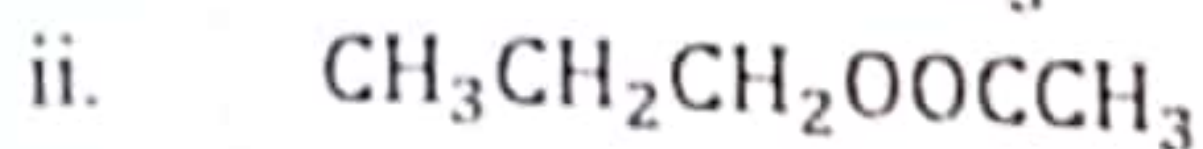
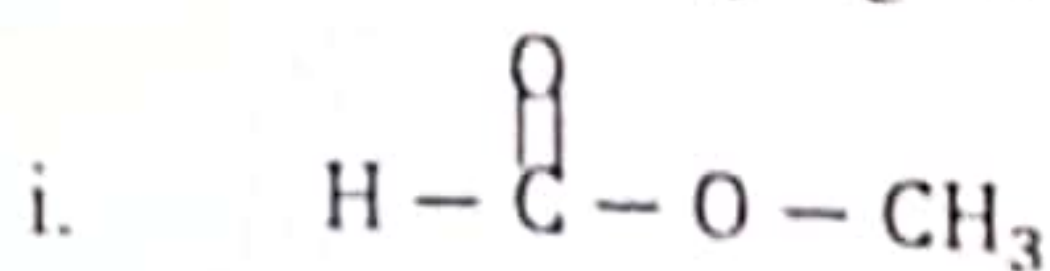
- Propyl ethanoate is used to produce pear flavour
- Octyl ethanoate is used to produce orange flavour

- **Pentyl ethanoate** is used to produce **banana flavour**
- **Ethyl butanoate** is used to produce **pineapple flavour**
- **Butyl ethanoate** is used to produce **apple flavour**
- **As fragrant**
 - Esters are used in perfumes and cosmetics to produce pleasant smell
- **Naturally occurring fats and oils are fatty acid ester of glycerol which are vital in the biochemistry of the body.**
- **Polycesters (polymers with ester group as functional group) are used to make plastics.**

PRACTICE EXERCISE 21

Problem 1

a. Name the following organic compounds:



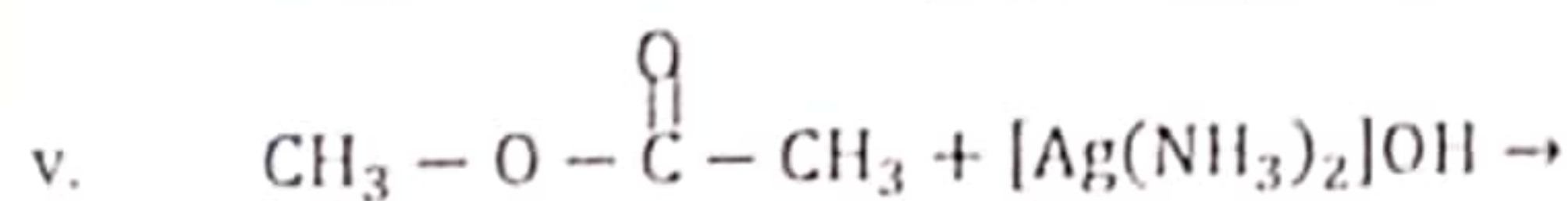
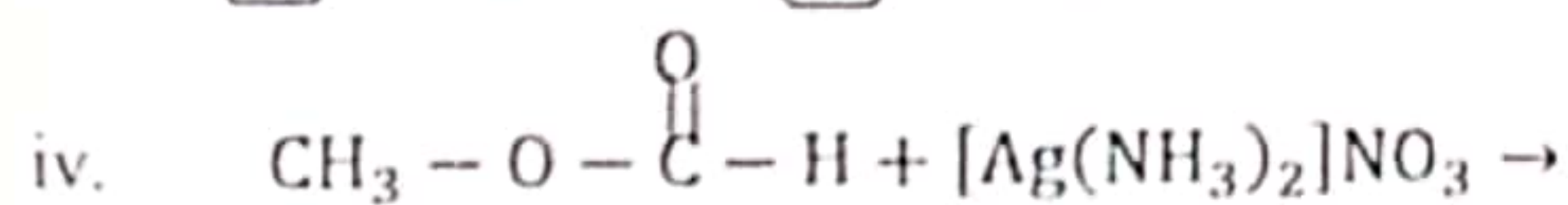
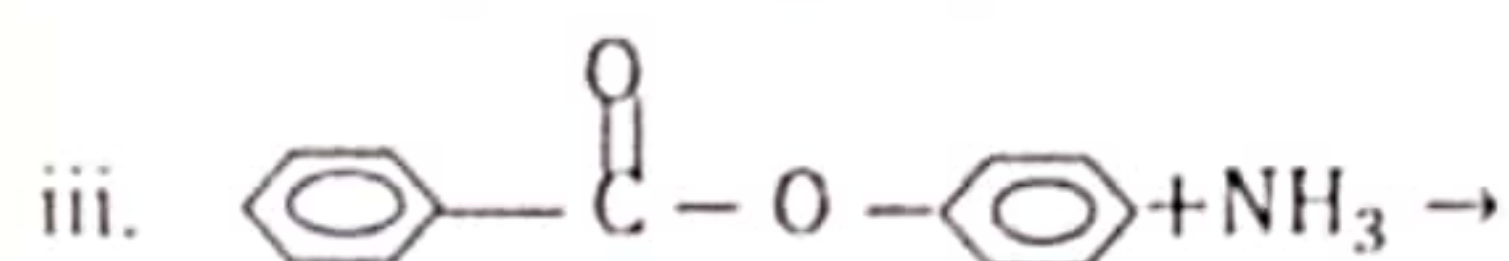
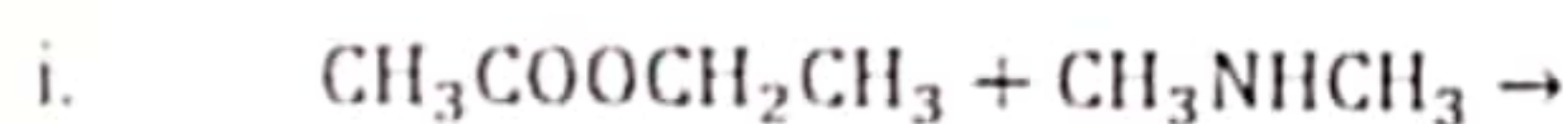
b. Give structures of three function isomers of propyl propanoate.

Problem 2

With the help of chemical equations give at least three different ways of preparing ethyl ethanoate.

Problem 3

Complete the following reaction equation:



Problem 4

Explain clearly how soap removes dirtiness.

Problem 5

Mention at least four uses of ester in the daily life.

Chapter 22

AMINES

INTRODUCTION

Amines are organic compound which are formed when at least one hydrogen atom of ammonia is replaced by alkyl or aryl group.

– Amines can be classified into three classes

- i) Primary (1°) amine
- ii) Secondary (2°) amine
- iii) Tertiary (3°) amine

i) Primary (1°) amine

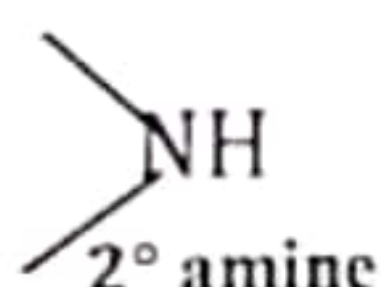
These are amines which are formed when only one hydrogen atom of ammonia is replaced by alkyl group or aryl group. Thus in primary amine nitrogen atom is directly bonded to two hydrogen atoms i.e $R - NH_2$ or $ArNH_2$.

ii) Secondary (2°) amine

These are amines which are formed when two hydrogen atom of ammonia are replaced by alkyl group or aryl group.

– The two hydrogen atoms may be replaced by one alkyl group and one aryl group or both alkyl groups or aryl groups. Thus for secondary amines, nitrogen atom is directly bonded to only one hydrogen atom.

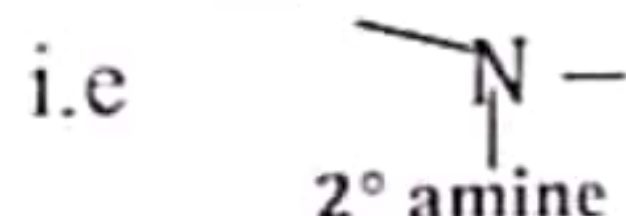
i.e



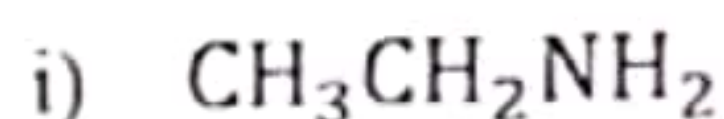
iii) Tertiary (3°) amines

These are amines which are formed when all three hydrogen atoms of ammonia are replaced by alkyl or aryl groups.

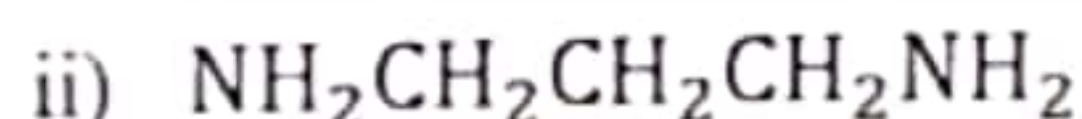
– The three hydrogen atoms may be replaced by alkyl or aryl groups only or any combination of the two (alkyl and aryl groups). Thus for tertiary amines there is no hydrogen atom which is directly bonded to nitrogen atom.



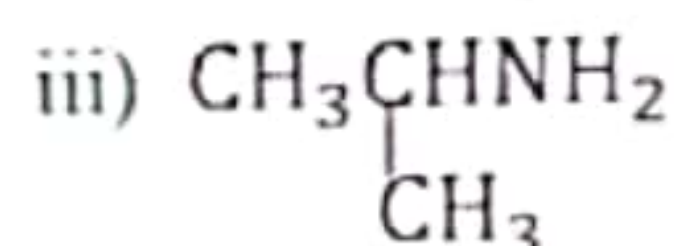
Nomenclature of amines



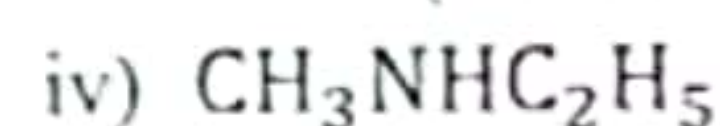
Name: ethanamine (common name: ethylamine)



Name: Propane – 1,3 – diamine (or 1,3 – propanediamine)



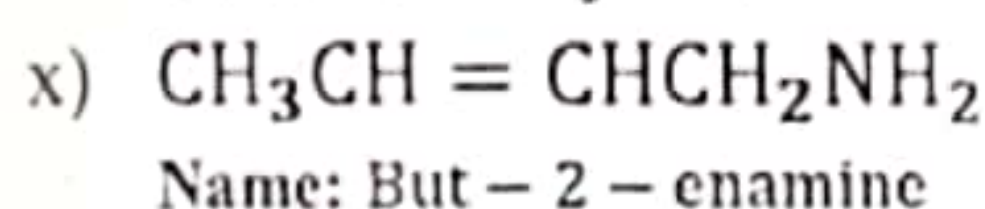
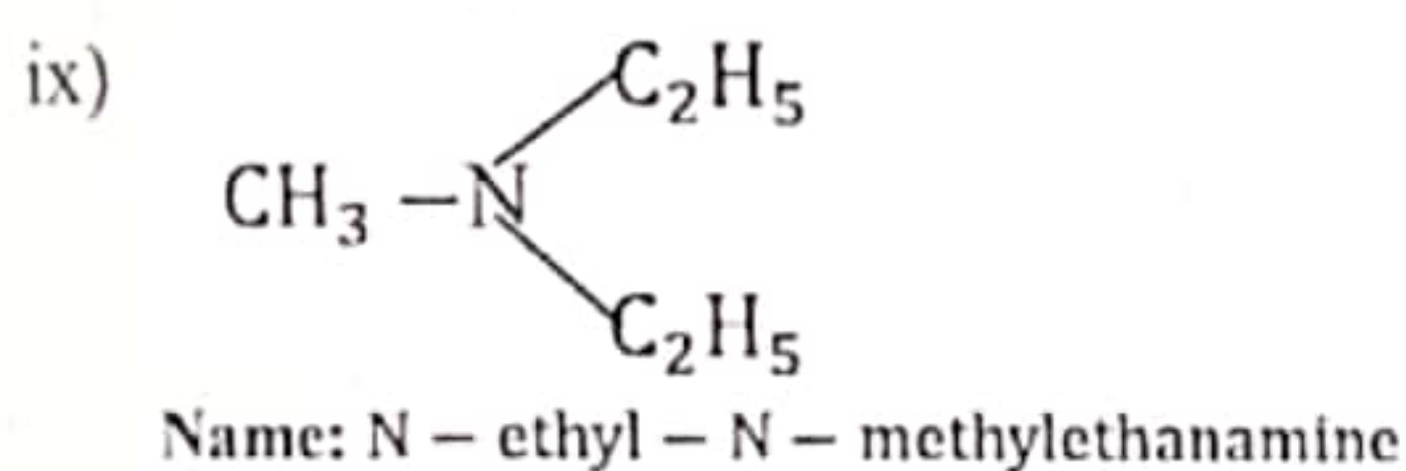
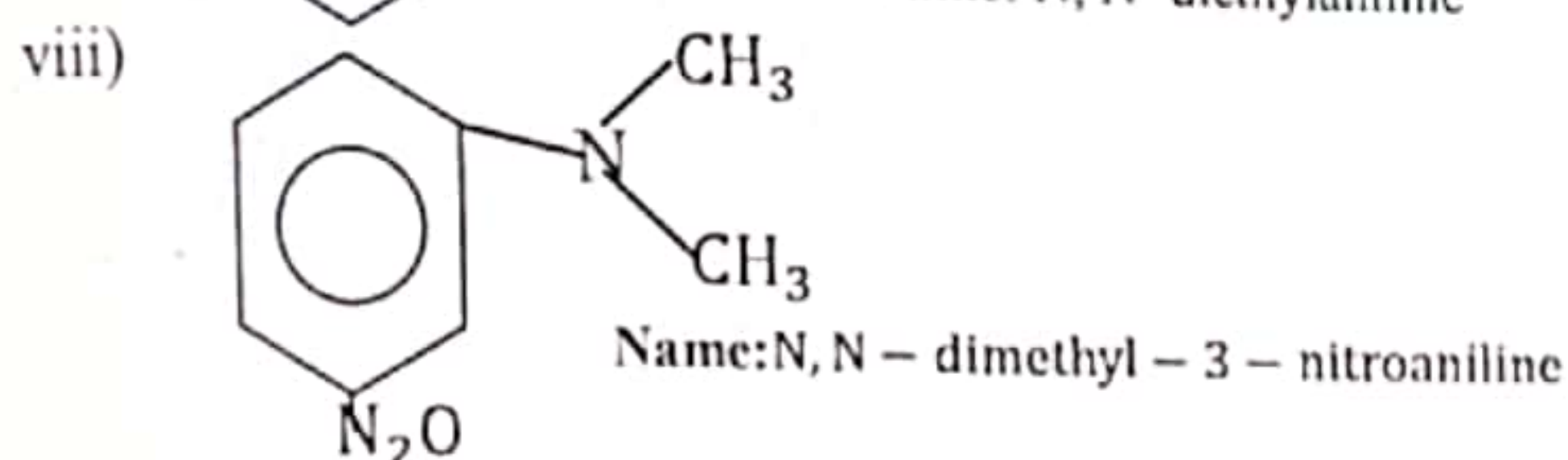
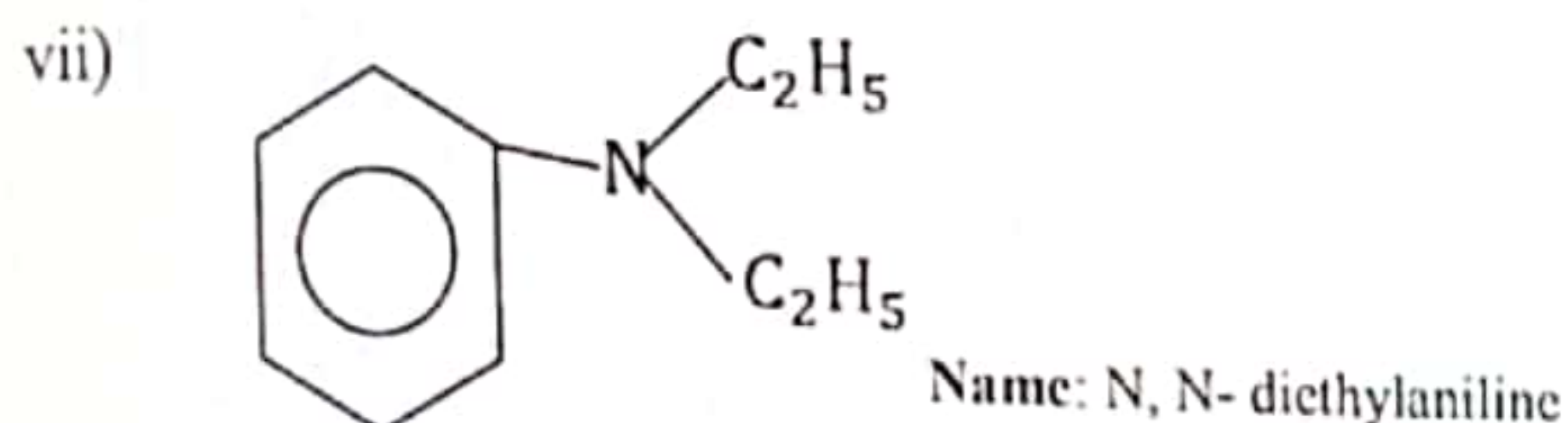
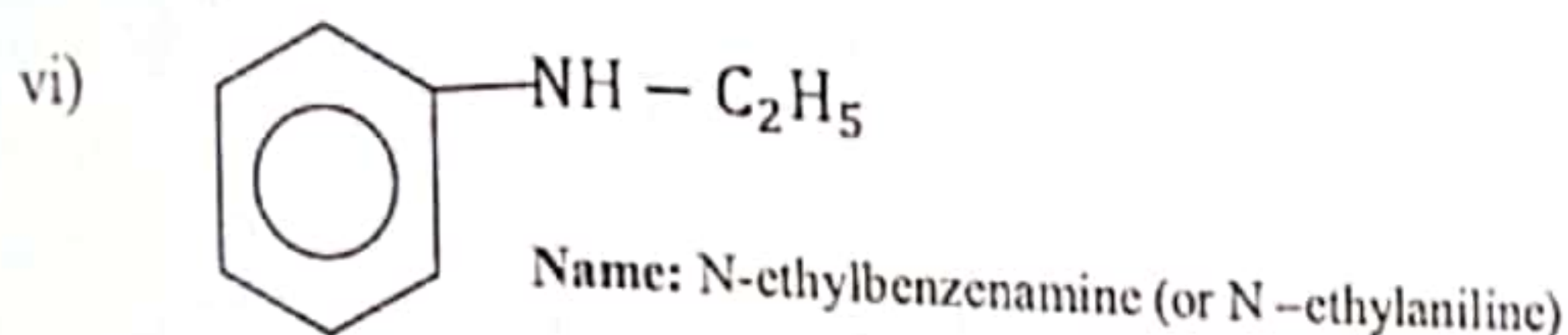
Name: Propan -2-amine (or 2-propanamine)
(Common name: isopropylamine)



Name: N-methylethanamine
(Common name: ethylmethanamine)



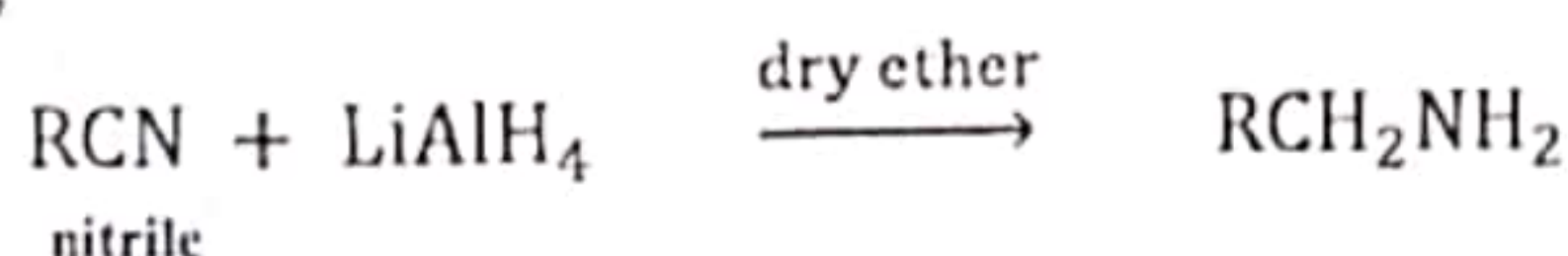
Name: Benzenamine
(Common name: phenylamine or aniline)



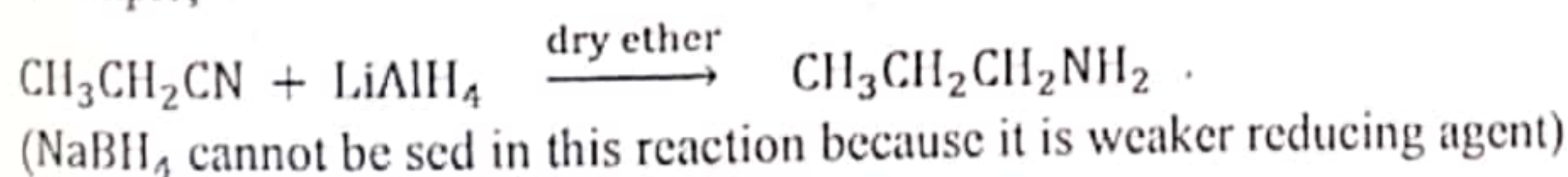
PREPARATION OF AMINES

a) Reduction of nitriles

Generally;

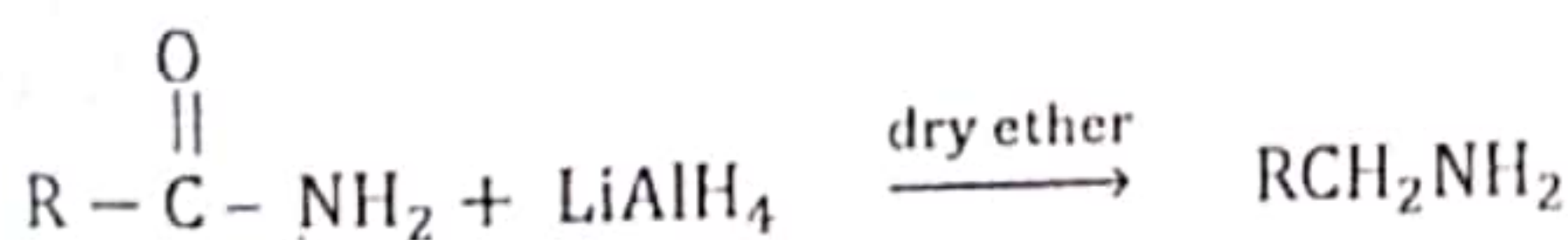


Example,

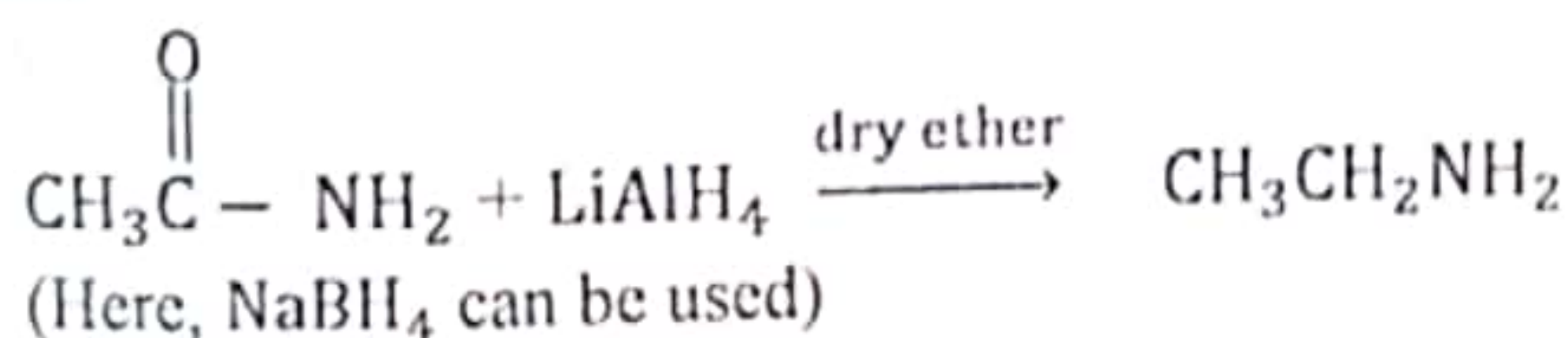


b) Reduction of amide

Generally;



Example,



c) Hofmann degradation

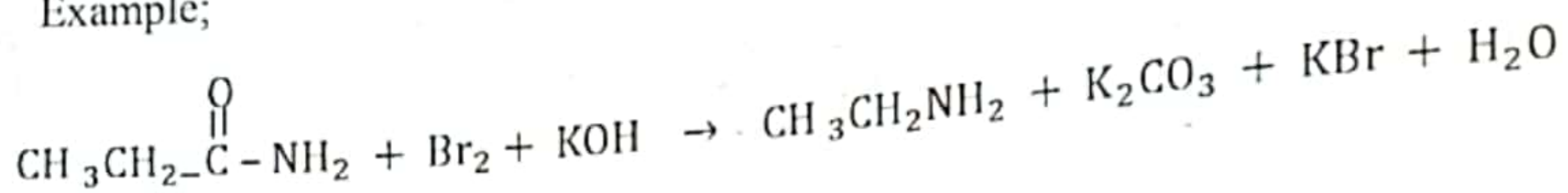
Hofmann degradation is the reaction between an amide and bromine under presence of an alkaline solution which involves the removal of carbonyl group from the amide resulting to formation of an amine.

Generally;



KOH may be used instead of NaOH

Example;



d) Reduction of nitroalkanes

Nitroalkane can be reduced to primary amines.

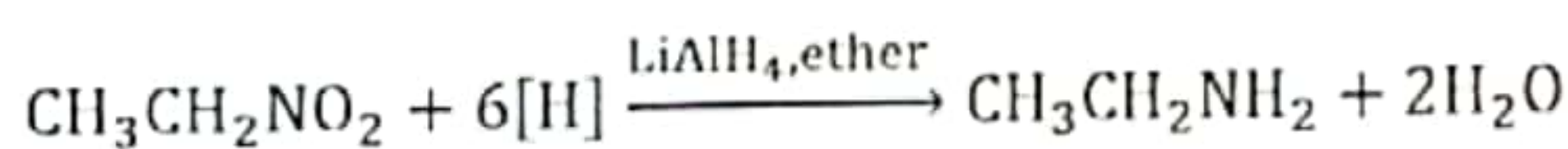
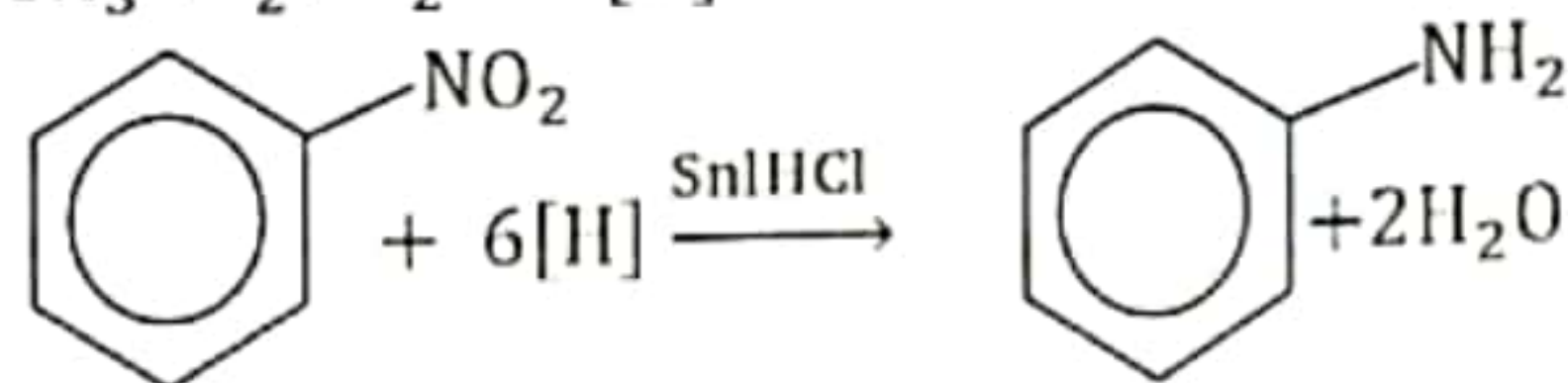
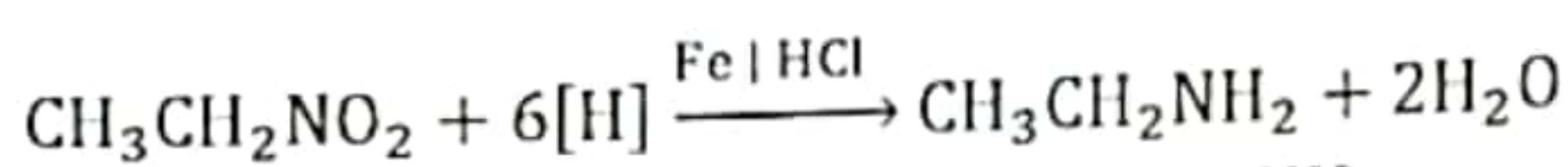
– Generally $\text{R}-\text{NO}_2 + 6[\text{H}] \rightarrow \text{RNH}_2 + 2\text{H}_2\text{O}$

Where $[\text{H}]$ represents nascent hydrogen or hydrogen from very strong reducing agent.

Thus $[\text{H}]$ can either come from:

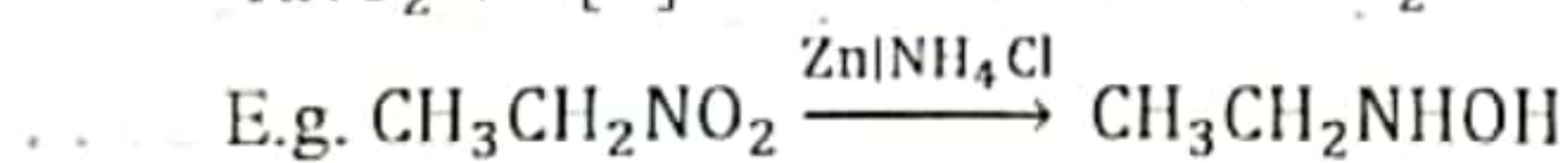
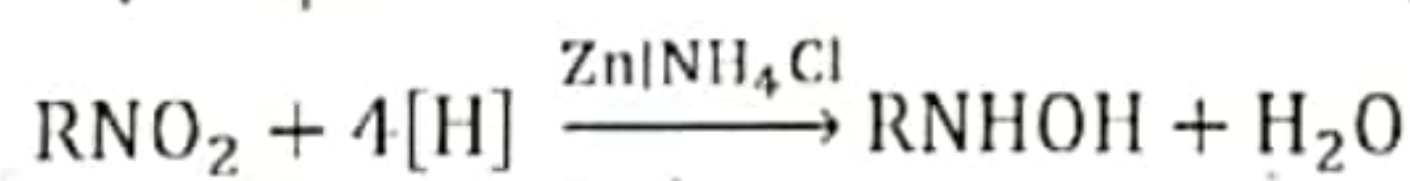
- $\text{Sn} | \text{HCl}$ mixture
- $\text{Fe} | \text{HCl}$ mixture or
- LiAlH_4 in presence of dry ether

For example;

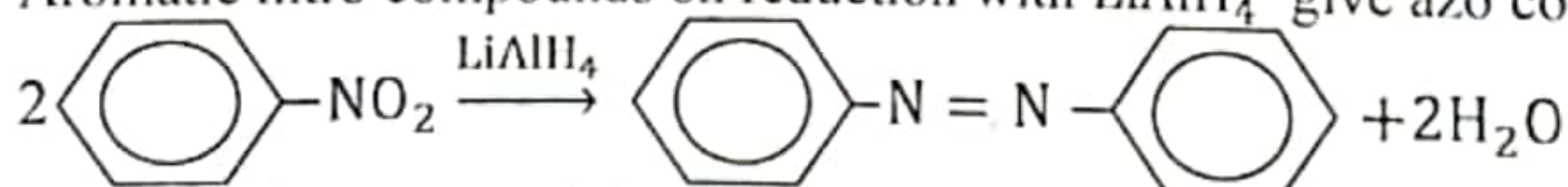


But:

- If $\text{Zn} | \text{NH}_4\text{Cl}$ mixture is used substituted hydroxylamine is formed.



- Aromatic nitro compounds on reduction with LiAlH_4 give azo compound.

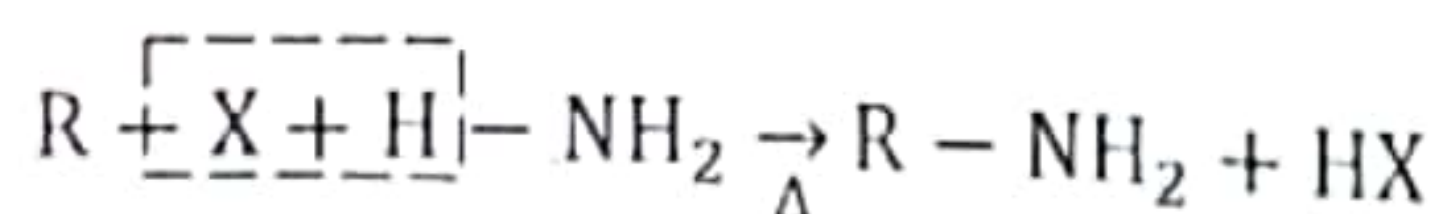


Note: NaBH_4 is not powerful reducing enough to reduce nitroalkane into amine.

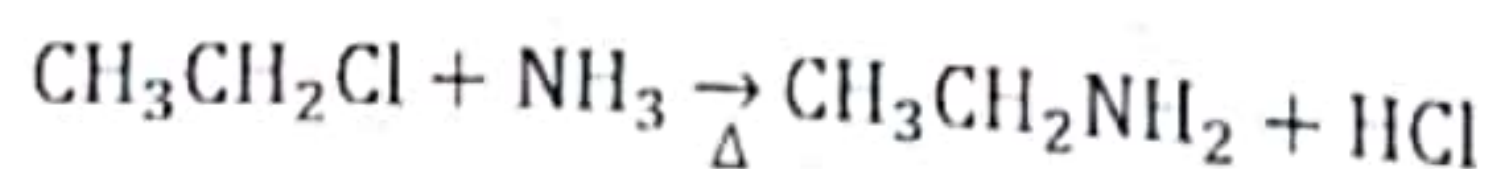
e) Reaction between haloalkane and ammonia

When haloalkane is heated with ammonia, amine is formed. The reaction takes place under alcoholic medium.

Generally;

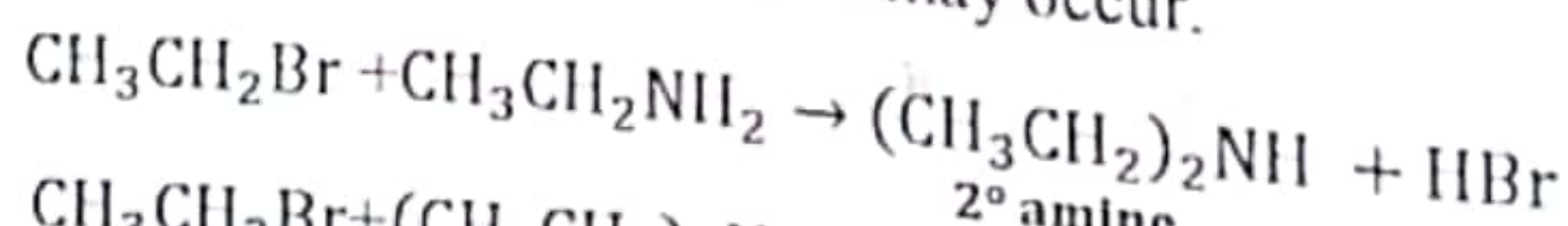


Example;

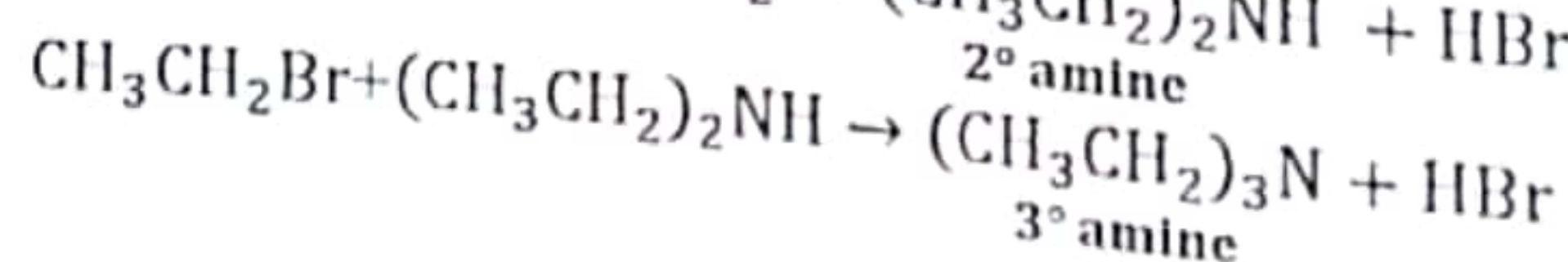


When haloalkane is in excess, a mixture of primary secondary and tertiary amines is formed because further substitution of hydrogen atoms from amine may occur.

That is

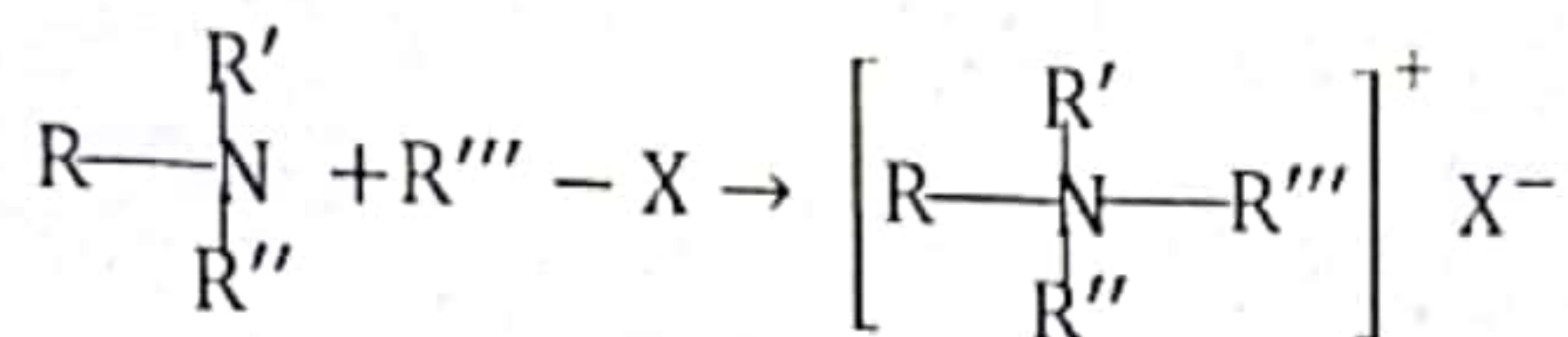


And



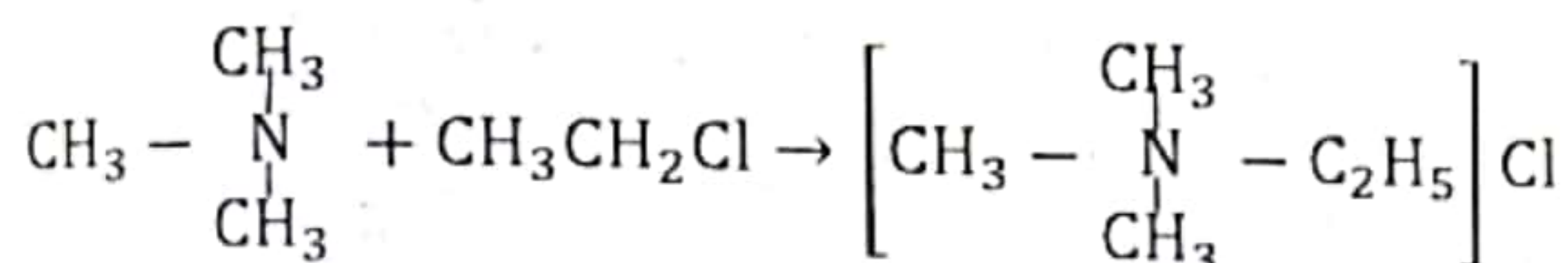
The reader should understand that:

Tertiary amine may undergo more alkylation to give solid quaternary ammonium salt.



(Compare with formation of ammonium halide like NH_4Cl . By equation $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ where H is just replaced by alkyl group).

For example;



Quaternary ammonium salts are very useful organic compounds

Are commonly used in;-

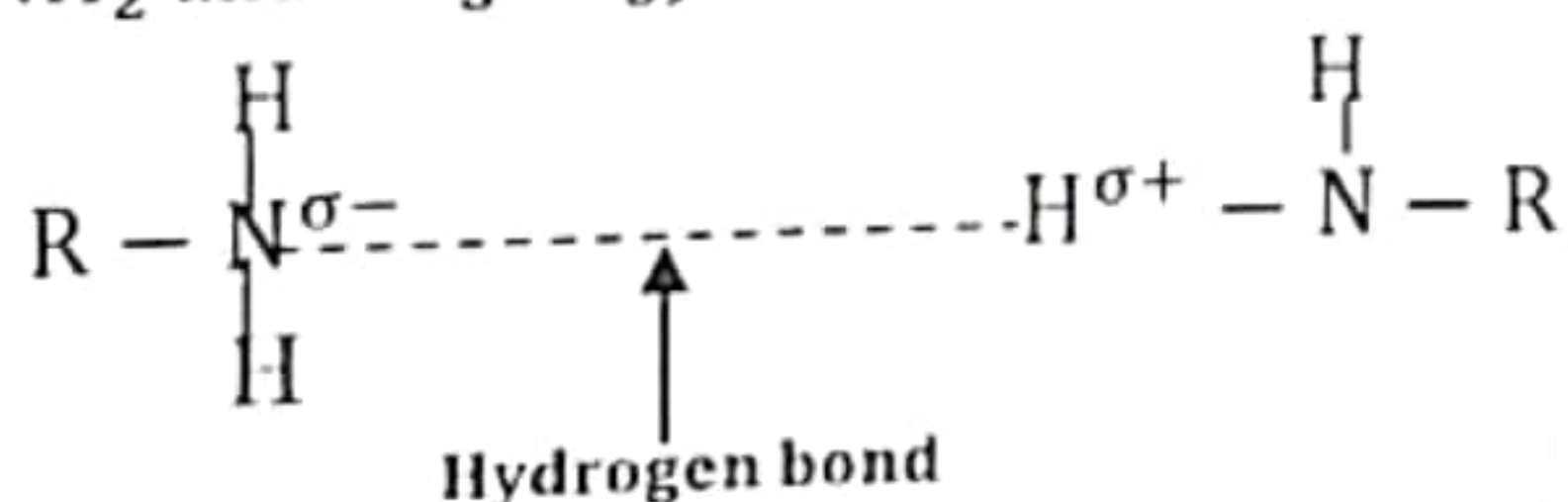
- Disinfectants
- Surfactants
- Fabric softeners
- Hair conditioners e.g. in shampoo

PHYSICAL PROPERTIES OF AMINES

i. Boiling point

Boiling points of amines are modified by presence of hydrogen bond between amine molecules

- Presence of hydrogen bond between amine molecules makes amines to have higher boiling point than corresponding members of hydrocarbon (hydrocarbon with similar molecular weight to that of amine like CH_3NH_2 and CH_3CH_3).



Compared to corresponding isomeric primary amine, secondary amine has slightly lower boiling point, *why this?* Because it has limited hydrogen bonding as the nitrogen in the secondary amine is in the middle of the chain (it surrounded by two alkyl group rather than at the end).

- For example although $\text{CH}_3\text{CH}_2\text{NH}_2$ and CH_3NHCH_3 have the same molecular weight (they are isomers to each other), boiling point of CH_3NHCH_3 is lower than that $\text{CH}_3\text{CH}_2\text{NH}_2$. That is all about boiling point of secondary amine, *what about tertiary amine?*

Nitrogen in tertiary amine has no hydrogen (all three hydrogen atoms of ammonia have been replaced by alkyl or aryl group) and therefore unlike in primary and secondary amine where there is hydrogen bonding there is no hydrogen bonding at all between molecules of tertiary amines.

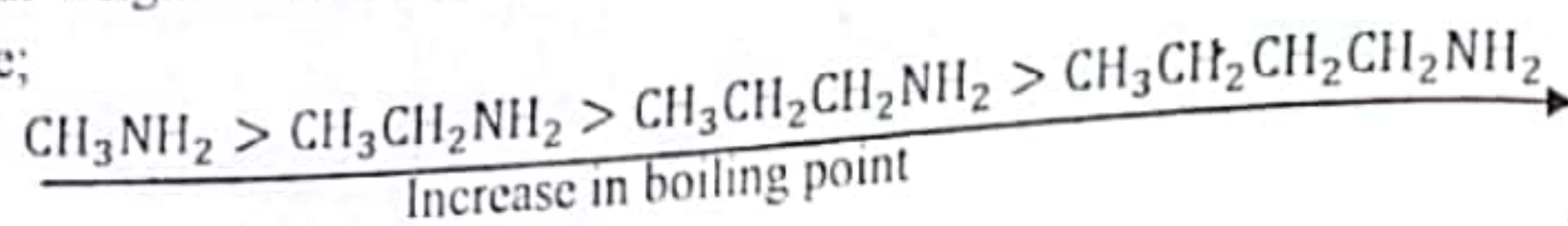
- This makes boiling point of tertiary amine to be much lower than that of primary and secondary amine for example, boiling point of propan-1-amine is 48.6°C while that of N,N-dimethylmethanamine (note the two compounds are isomers) is only 3.5°C !
- To summaries the boiling point of primary secondary and tertiary amine is according to the following order

Primary (1°) amine > secondary (2°) amine > Tertiary (3°)

Ngaiza's series of advanced chemistry

For amine of the same class, boiling point increase with an increase in the length of carbon chain that is as the molecular weight increase due to increase in Van-der-Waals force of attraction.

– For example;



ii. Solubility

Generally amines are soluble in water due to their ability to make hydrogen bonding with water molecules.

Interesting!

Although the tertiary amines do not have hydrogen atom attached to the nitrogen and therefore cannot form hydrogen bonds between themselves, they can form hydrogen bonds with water molecules just using lone pair on the nitrogen and positively polarised hydrogen of neighbour water molecule.



- Like in alcohols, solubility of amine in water decreases as the length of carbon chain increases.
- Amine are also soluble in organic solvents like ether and alcohols

iii. Smell

Gaseous amines (methylamine and ethylamine) have characteristic ammonia smell (pungent smell which smell like concentrated urine) while liquid amines have fishy smell (there is N, N-dimethylmethanamine and N-methylmethanamine in fish).

iv. Physical state

- Lower members of aliphatic amines (methylamine and ethylamine for primary amines) are gases while higher members are liquid.
- For aromatic amines, lower members are liquid but higher members are solid.

Very important to understand that:

- In alcohol there are two lone pairs in oxygen thus making alcohol to have two positions for making hydrogen bonding while in amine only one lone pair is present in the nitrogen.
- Thus make alcohol to exhibit stronger hydrogen bonding and therefore greater modification on physical properties in alcohol than in amines.

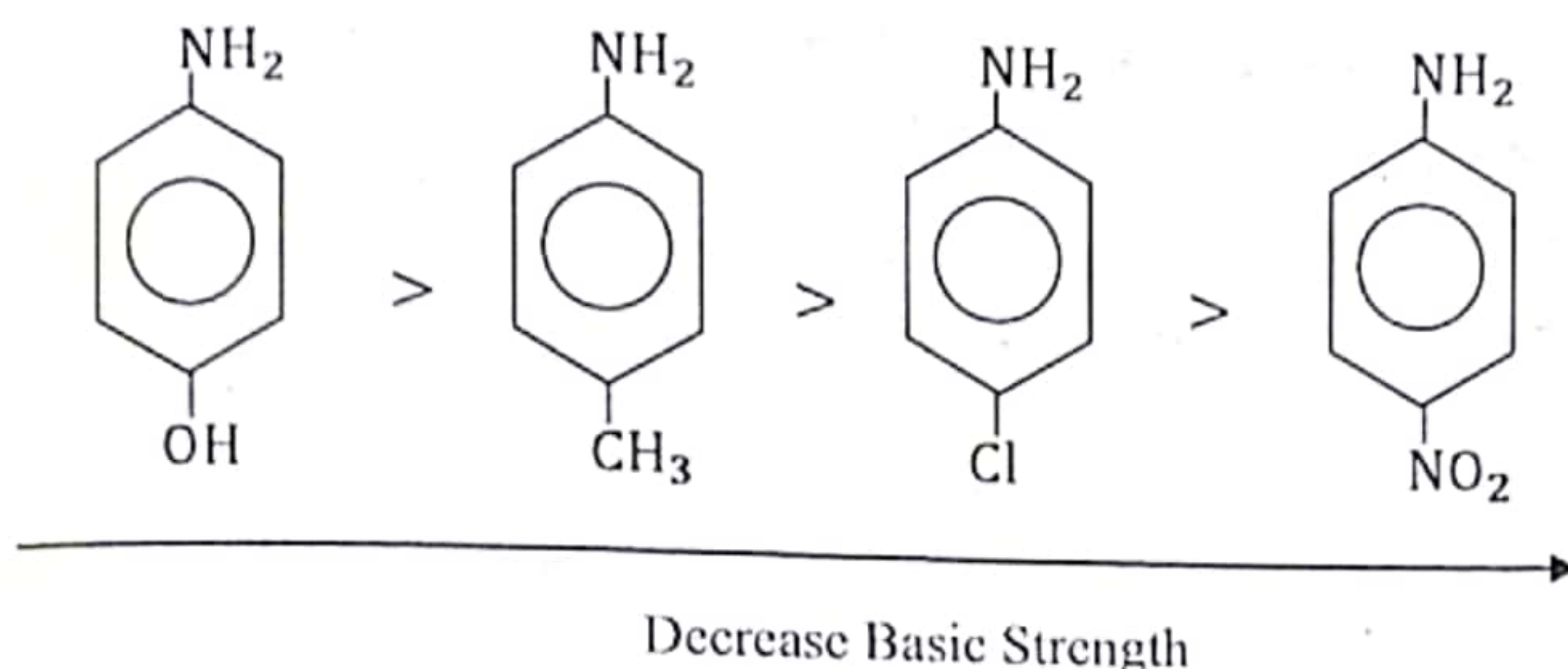
Below are few practical evidences of the above fact:

- Boiling points of alcohols is greater than those of corresponding members of amines. For example $\text{CH}_3\text{CH}_2\text{OH}$ is liquid at room temperature while $\text{CH}_3\text{CH}_2\text{NH}_2$ is gas.
- Solubility of alcohols in water is greater than those of corresponding members of amines (in fact larger amines with more than six carbons are essentially insoluble in water).

Basic behaviour of amines

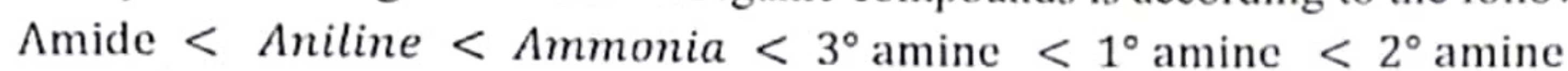
Basic characteristics of amines are clearly explained by the presence of lone pair in nitrogen thus making it proton acceptor (electron donor) and hence amines are good Lewis base.

- Basic strength of aliphatic amine has clearly discussed in introduction of organic chemistry. For aniline, basic strength depend on the type of substituent group in Benzene ring. If the substituent is activator then the amine will be stronger base and if it is deactivator will be the weak base.



In comparison to amides, amines are more basic due to the fact that; structure of amide favours occurrence of mesomerism which reduces the ability of lone pair electrons of nitrogen to be donated to a Lewis acid (lone pair participates in mesomerism). Moreover, oxygen in a carbonyl group ($-\text{CONH}_2$) causes a negative inductive effect, e.g. $\text{CH}_3\text{CH}_2\text{NH}_2$ is more basic than CH_3CONH_2 .

- Generally, the basic strengths of various organic compounds are according to the following order:



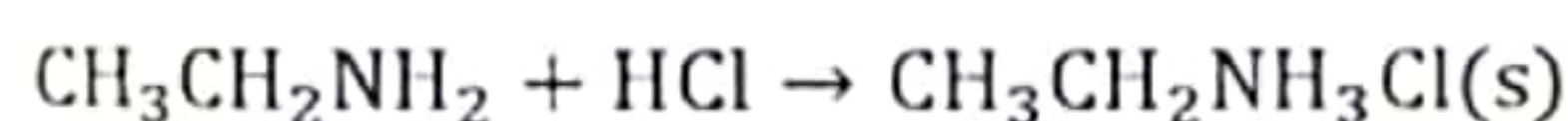
Least basic

Most basic

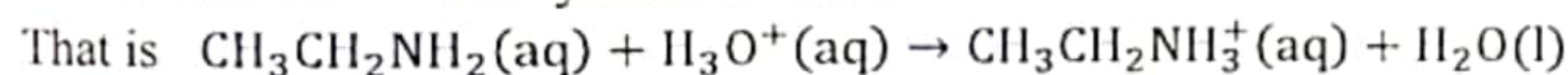
CHEMICAL REACTION OF AMINES

Amine as a base

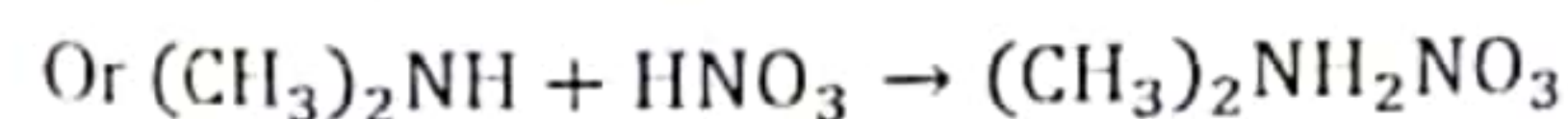
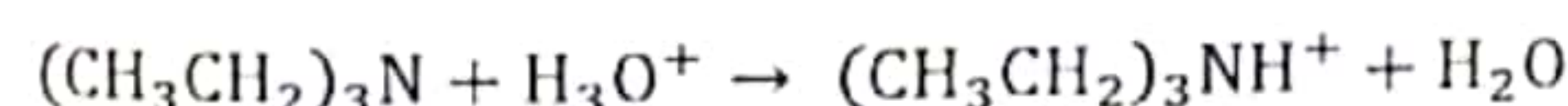
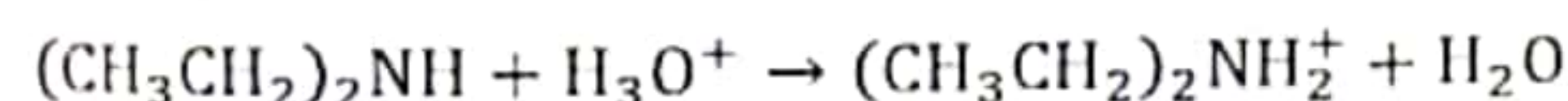
As a base, ammonia can react with an acid like HCl. For example, ethanamine reacts with hydrogen chloride gas to produce dense white fumes of ethylammonium chloride like ammonia does to HCl(g).



- It also reacts with hydronium ion in the acid-base neutralisation reaction.



Similarly



Dimethylammonium nitrate

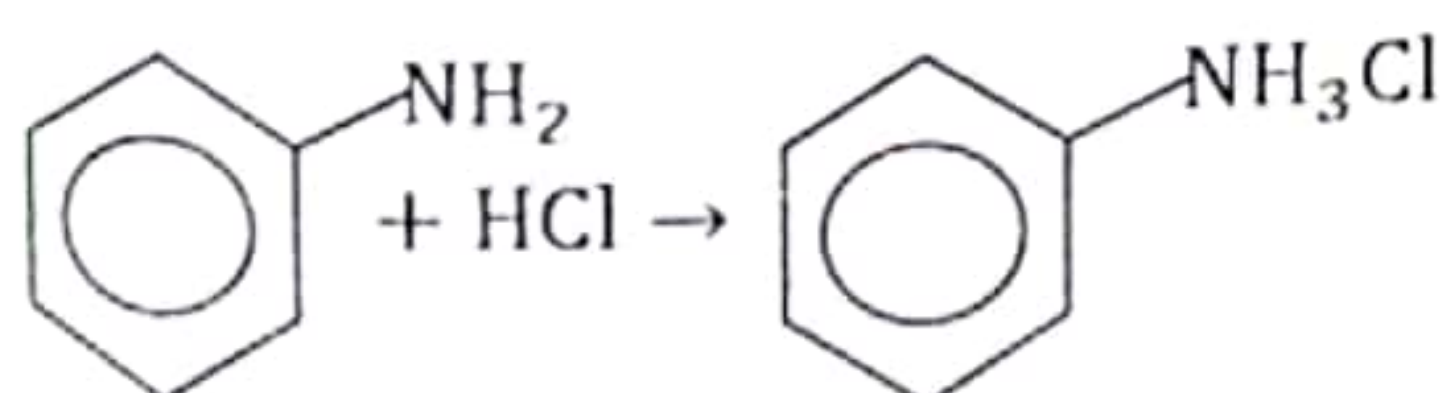
Very nice to hear!

Basic character of amine explains why lemon and vinegar are commonly used to remove smell in very smelly fish.

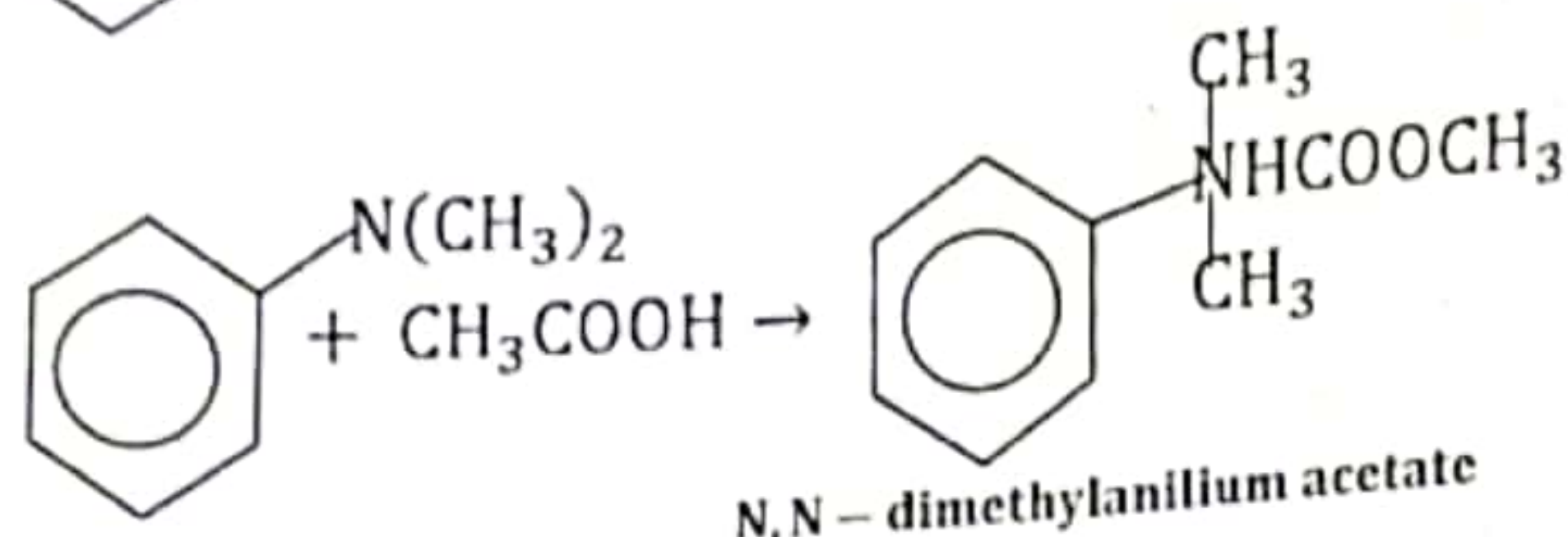
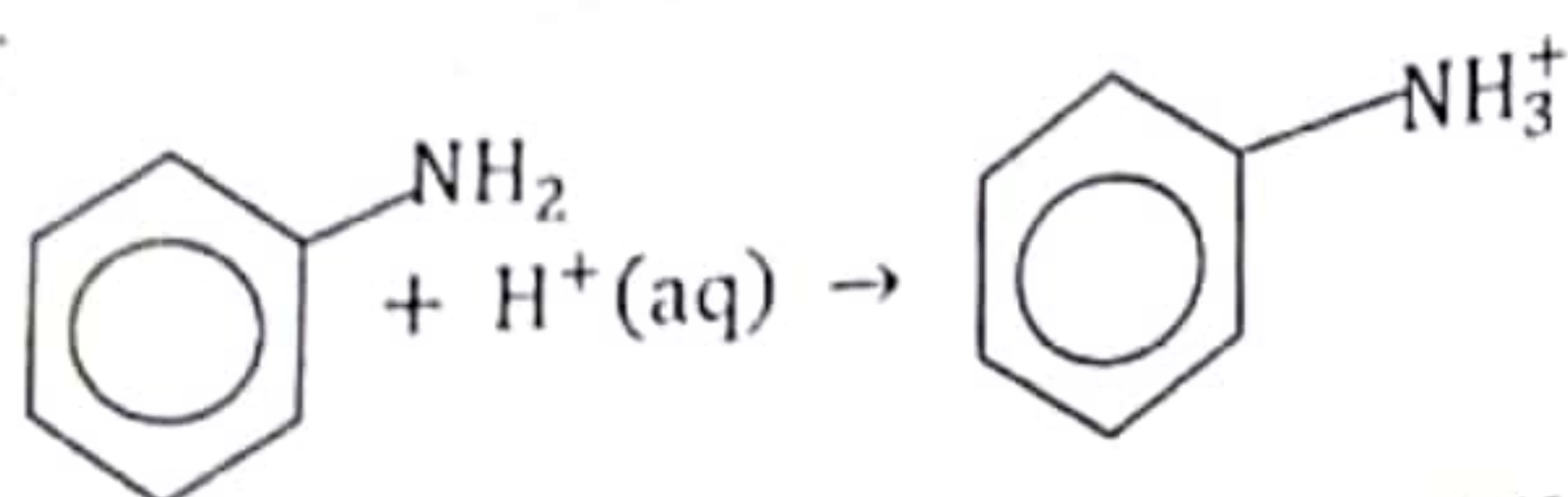
- This is simply because fishy odour is the result of presence of amine which is basic. Lemon and vinegar being acidic in nature neutralise amine present in the fish in acid-base neutralisation reaction.

Reaction of aniline with acid

Aniline reacts with acids like hydrochloric acid in exactly the same way as aliphatic amines.



Or

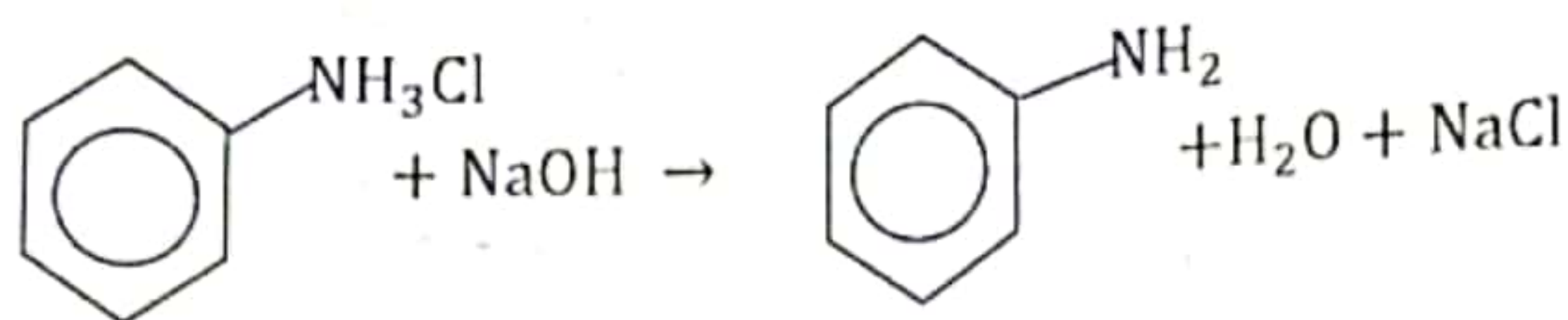


N,N - dimethylanilinium acetate

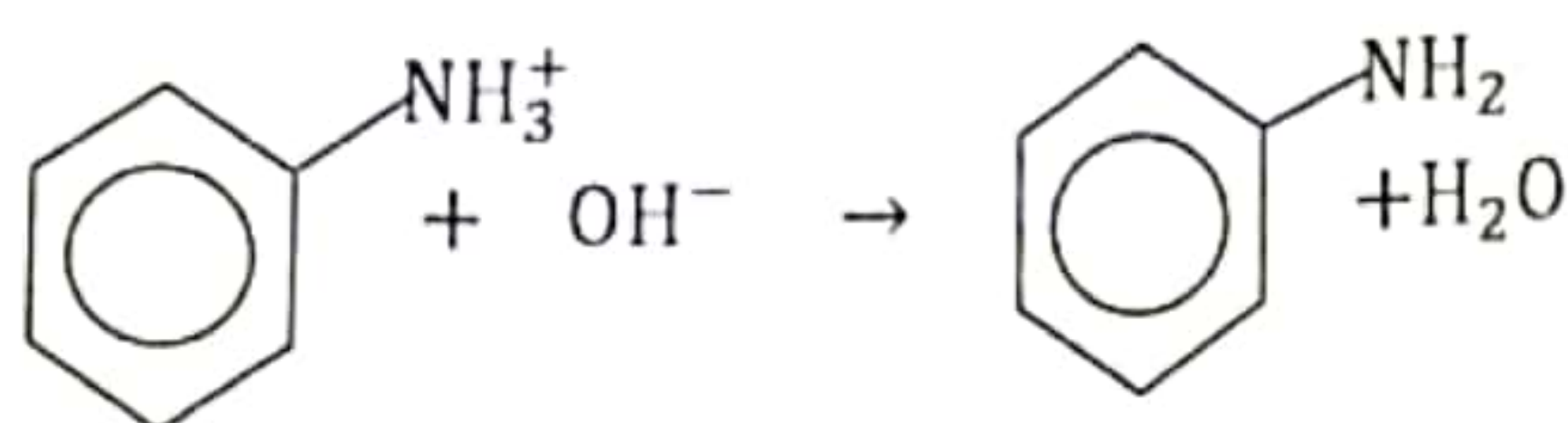
It should be noted that:

The phenylammonium ion (or alkylammonium ion) can be converted back to amine by treating it with strong base like NaOH.

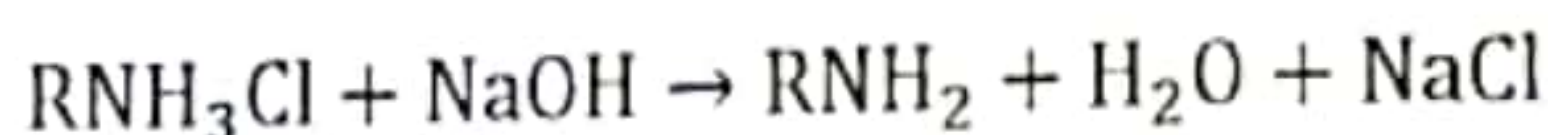
For example:



Or ionically



Similarly;

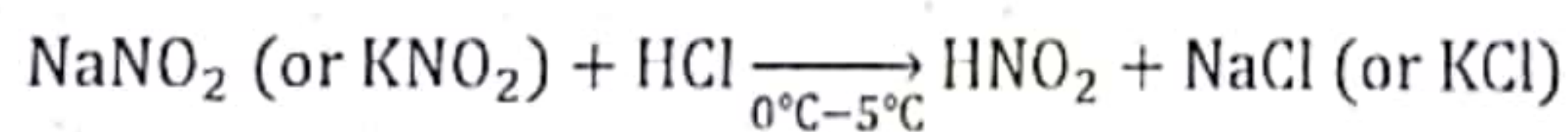


Reaction of primary amines with Nitrous acid

Primary amine reacts with nitrous acid to form alcohol and nitrogen gas which appear as gas bubbles.

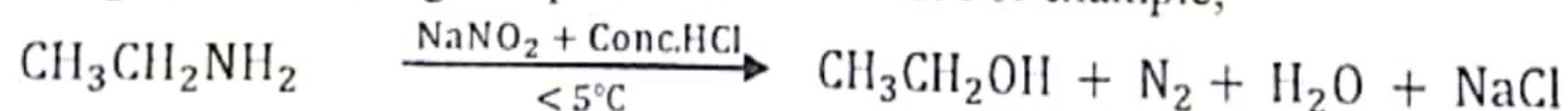


Because nitrous acid is unstable, it is prepared immediately before its use as per equation;



(H_2SO_4 may be used instead of HCl and the equation becomes $\text{NaNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_2 + \text{NaHSO}_4$)

- So don't be confused because sometime you may be given NaNO_2 | HCl mixture instead of HNO_2 ! The same organic product is obtained. For example;



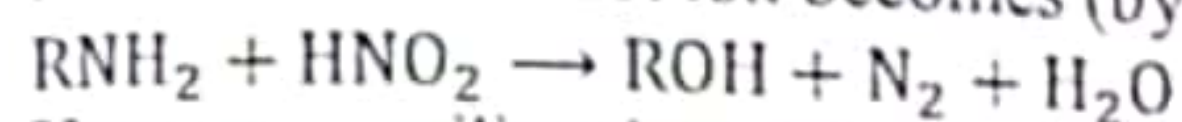
The reaction takes place via formation of diazonium cation.

That is $\text{RNH}_2 + \text{HNO}_2 \rightarrow \text{R}-\text{N}^+\equiv\text{N} + \text{H}_2\text{O} + \text{OH}^- \dots \dots \dots$ (i)

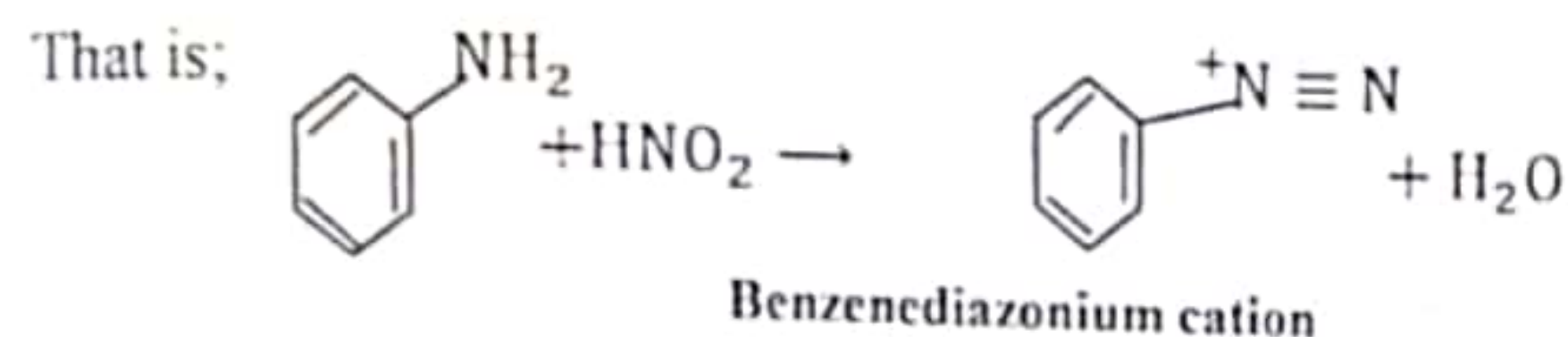
Then $R - ^+N \equiv N \rightarrow R^+ + N_2(N \equiv N) \dots \dots \dots (ii)$

Finally $R^+ + OH^- \rightarrow ROH \dots \dots \dots (iii)$

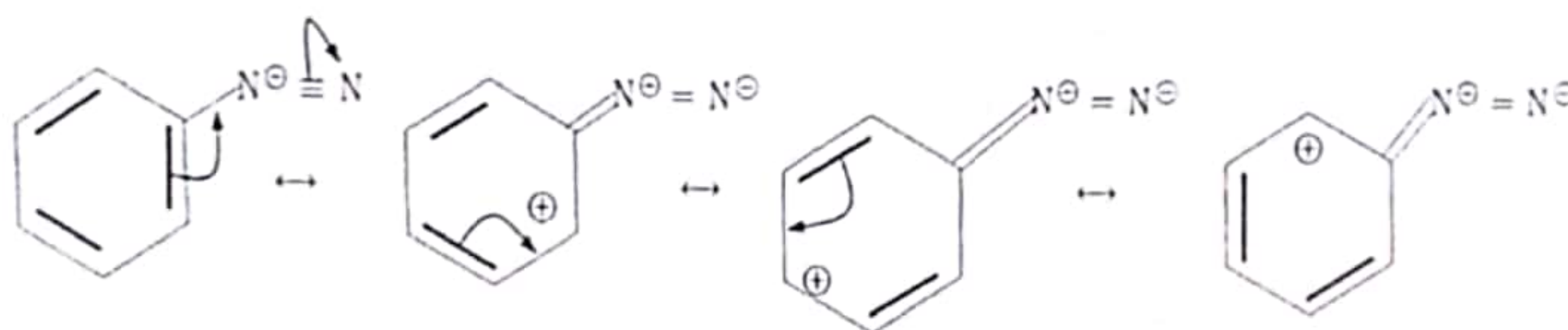
And the overall reaction becomes (by taking (i) + (ii) + (iii))



However aniline does not react in this way because it can form stable diazonium cations (at temperature below 5 °C as result of stabilisation brought about by mesomerism)

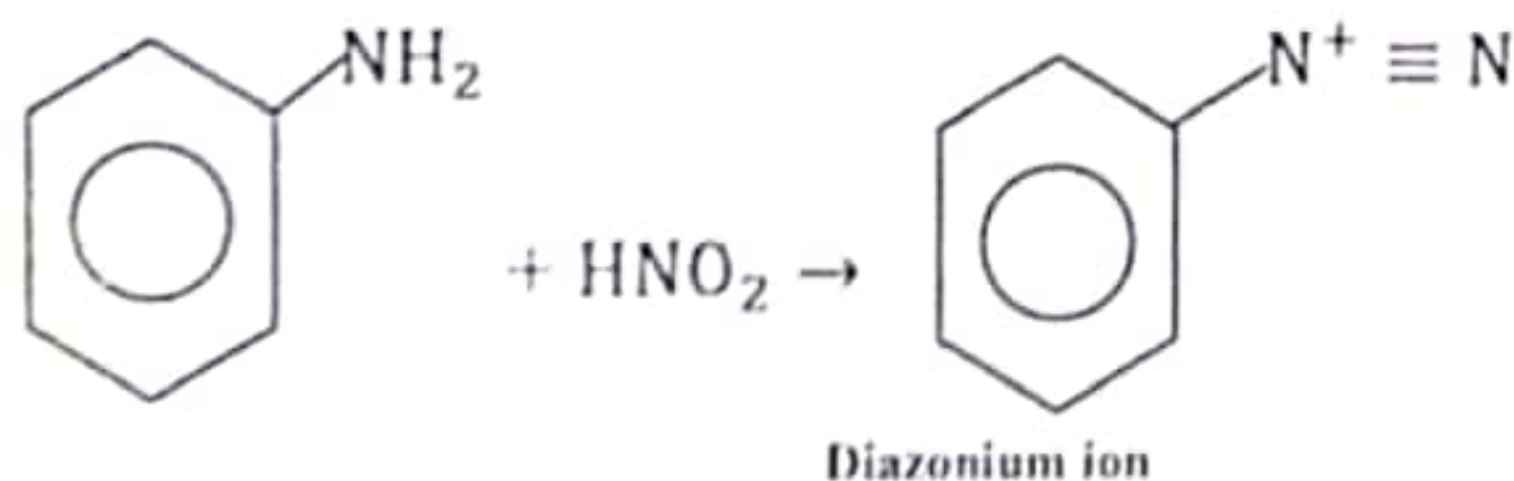


Then stabilisation of the benzenediazonium ion by mesomerism as follows:

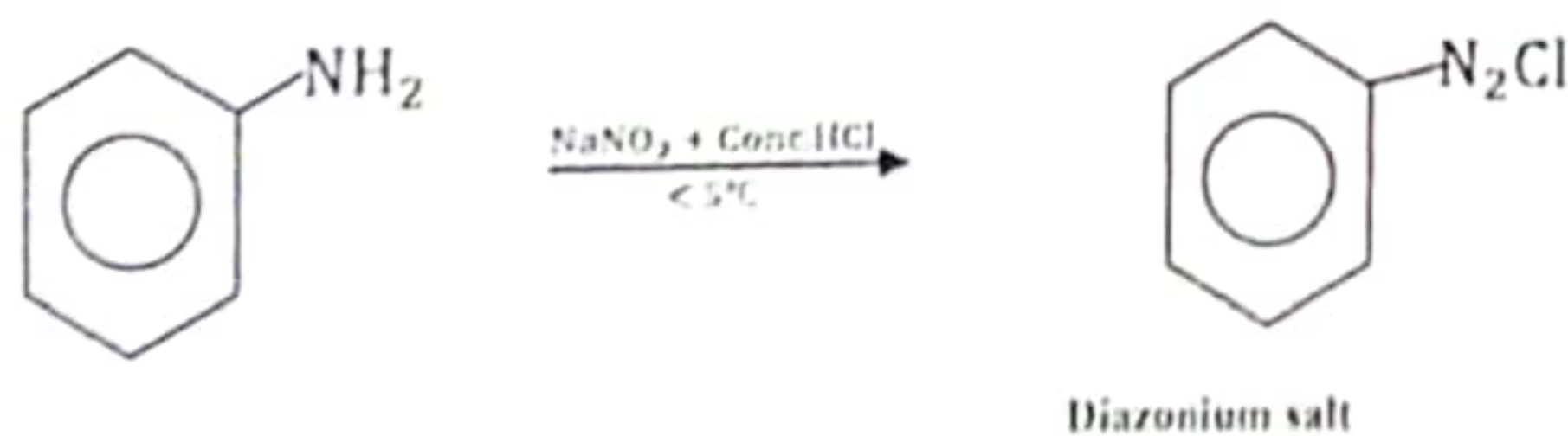


- This resonance accounts for the stability of the diazonium ion.

So the aniline does not form alcohol, instead it tends to form diazonium ion (or diazonium salt) and process is known as **diazotisation**.



OR



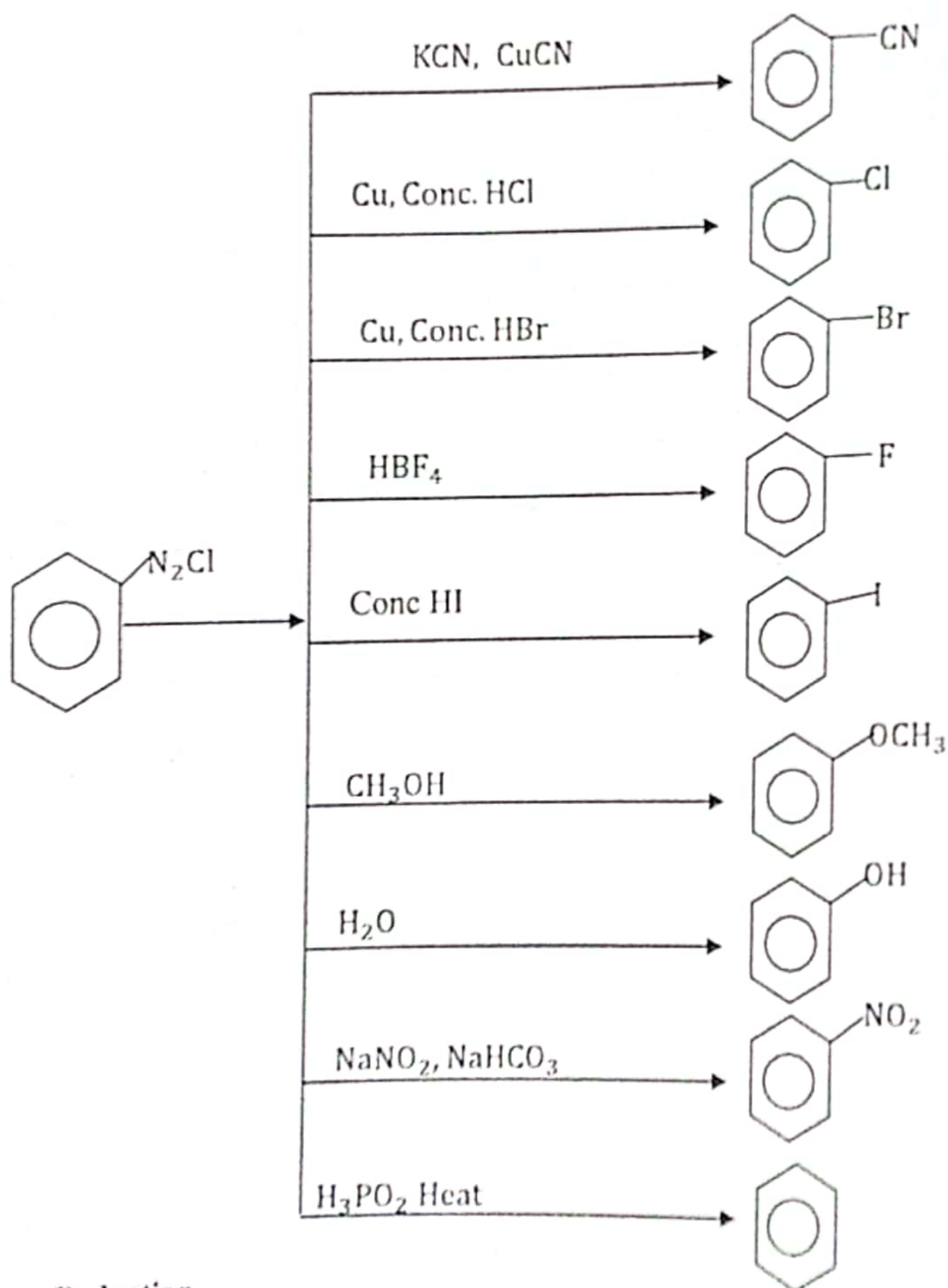
The reaction is very important in distinguishing between aliphatic primary amine and aniline (phenylamine) as aliphatic primary amine give bubbles of nitrogen gas while aniline does not.

Benzenediazonium chloride is very useful in synthesizing many organic compounds. It undergoes three types of reaction:

- Substitution reaction
- Reduction reaction and
- Coupling reaction

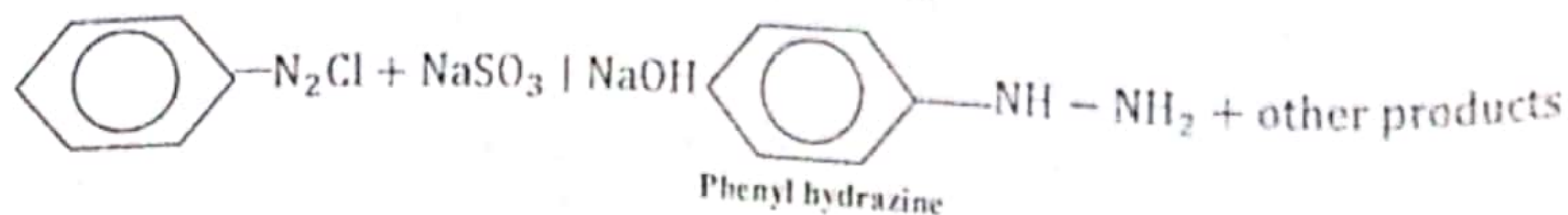
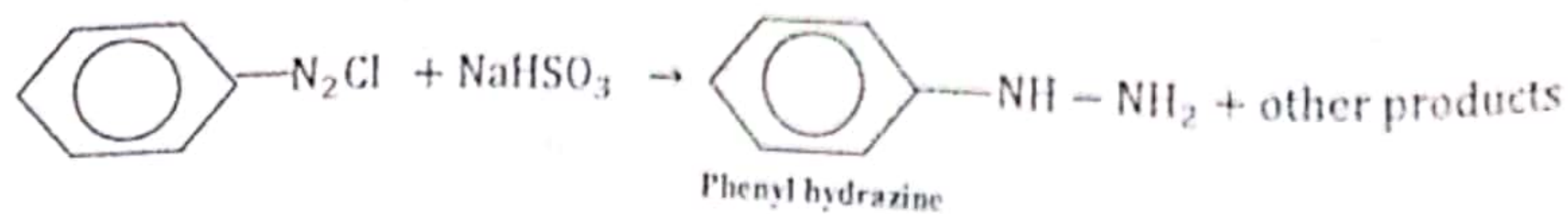
1. Substitution reactions

In these reactions, nitrogen is evolved and the diazonium group is substituted by another atom or group of atoms as shown below:



2. Reduction

Benzenediazonium chloride undergoes reduction with compounds like sodium to give bisulphate to give phenyl hydrazine.



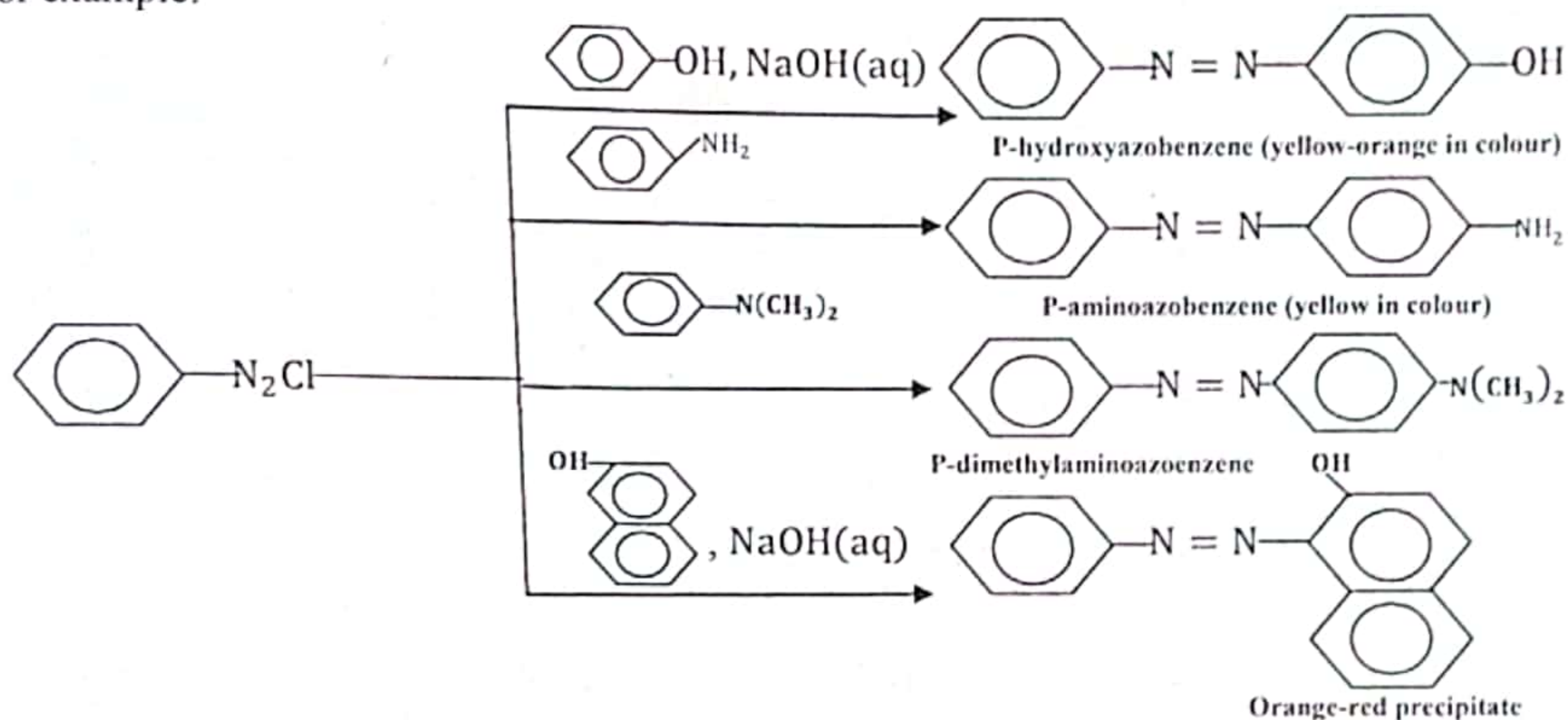
Where NaHSO_3 is produced from $\text{NaSO}_3 + \text{NaOH}$ mixture in the reaction

3. Coupling reaction

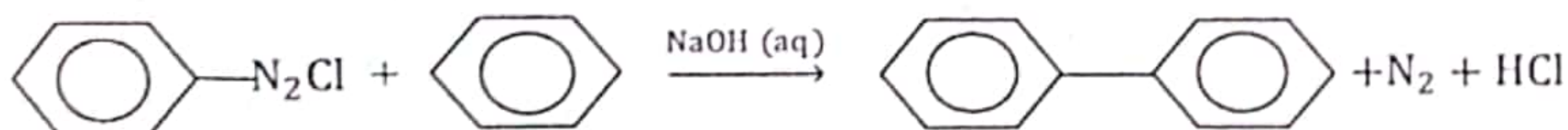
Benzenediazonium chloride couples with strongly activated aromatic compounds such as phenols or amines.

- The products of such reactions are azo compounds containing $-N=N-$ bond in the molecule.
- Coupling occurs at para carbon with respect to position of hydroxyl or amino group but if the para position is blocked, the coupling will take place at the ortho position (remember OH and NH_2 groups are ortho-para directors).

For example:



Also;



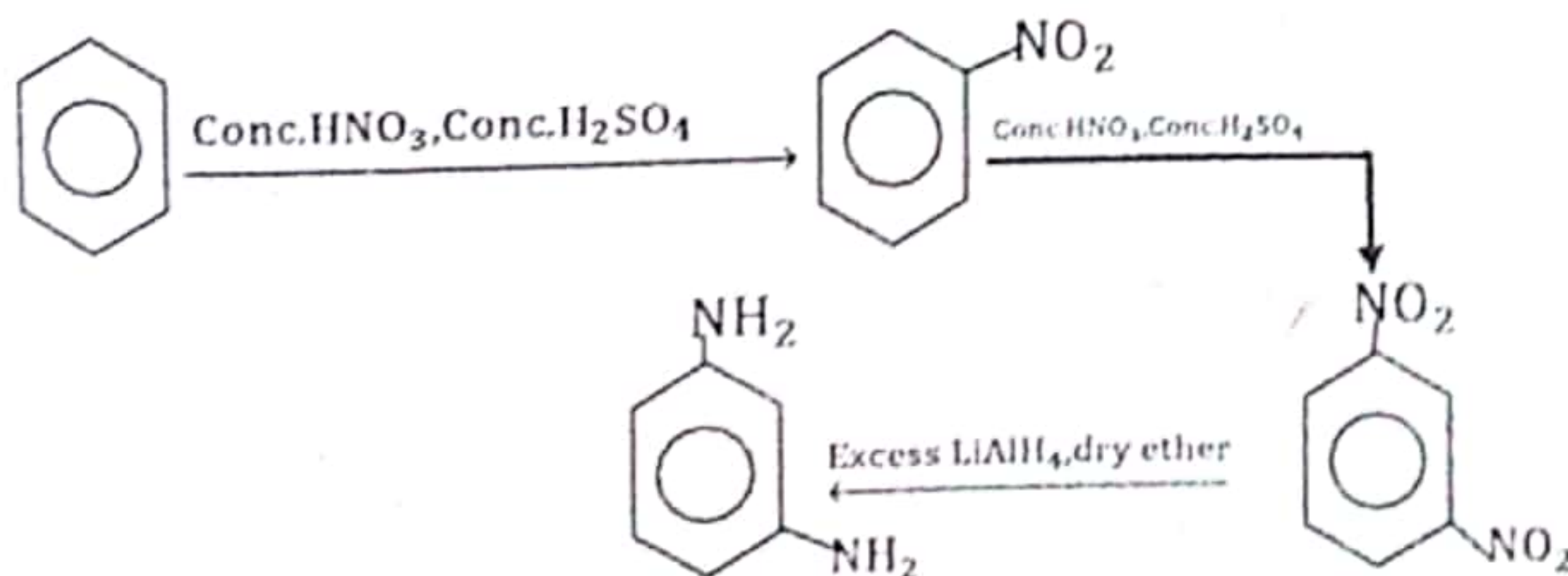
Example

Convert:

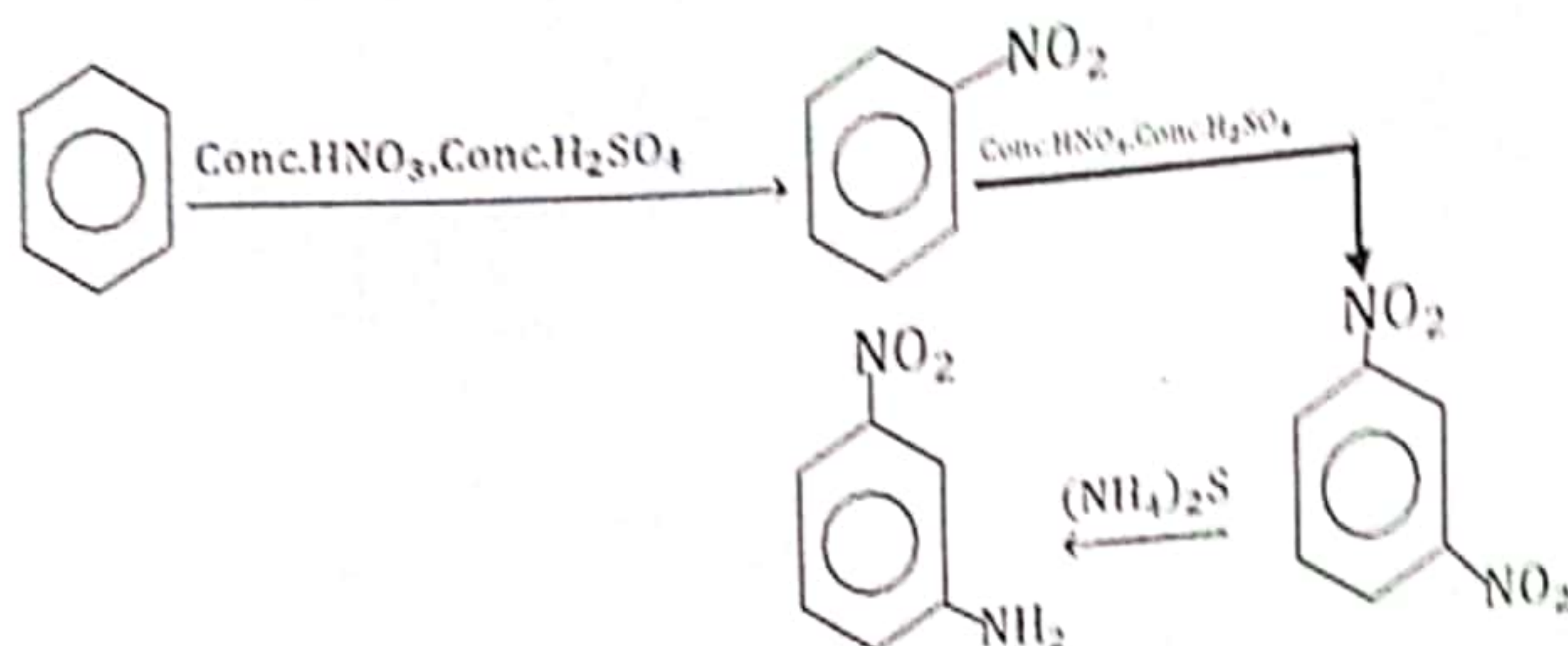
- Benzene into m-aminoaniline
- Benzene into m-nitroaniline
- Nitrobenzene into toluene
- Nitrobenzene into benzoic acid

Solution

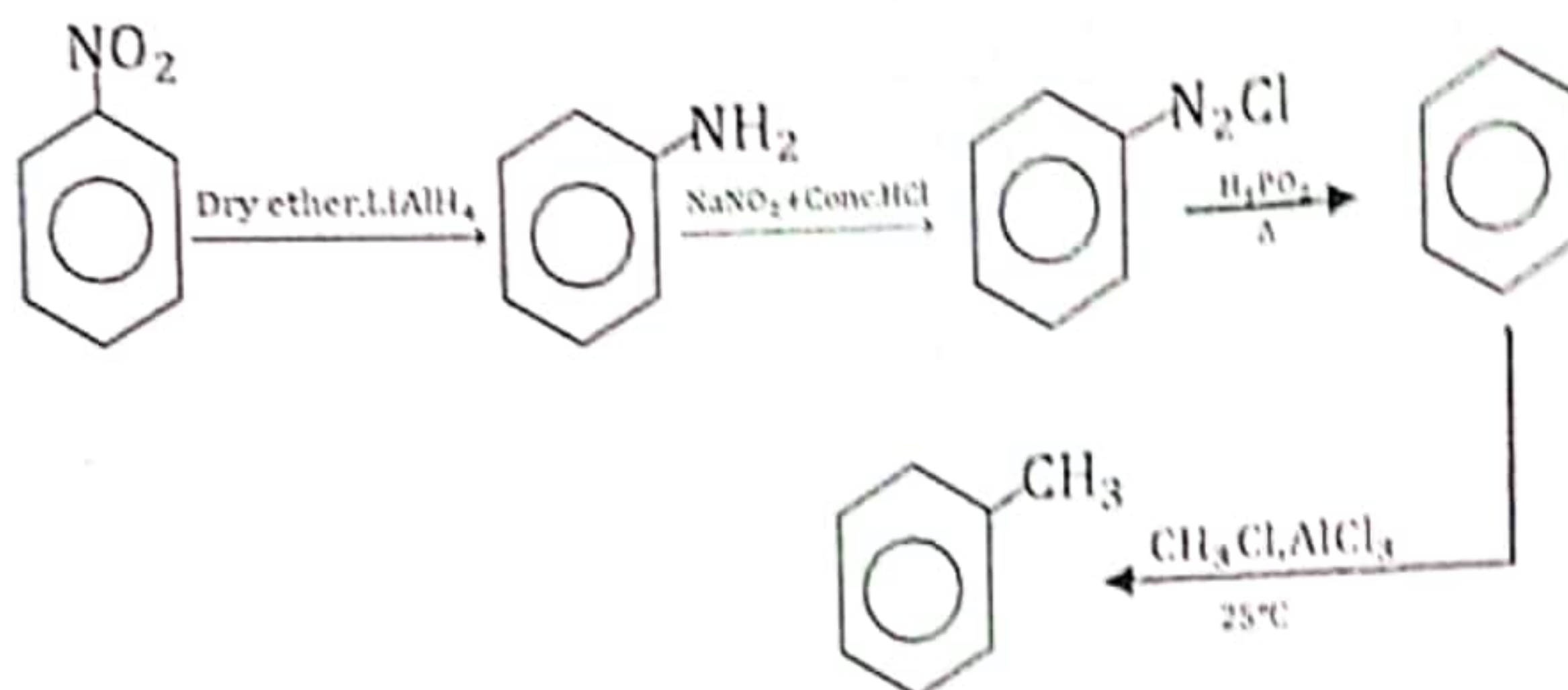
i)



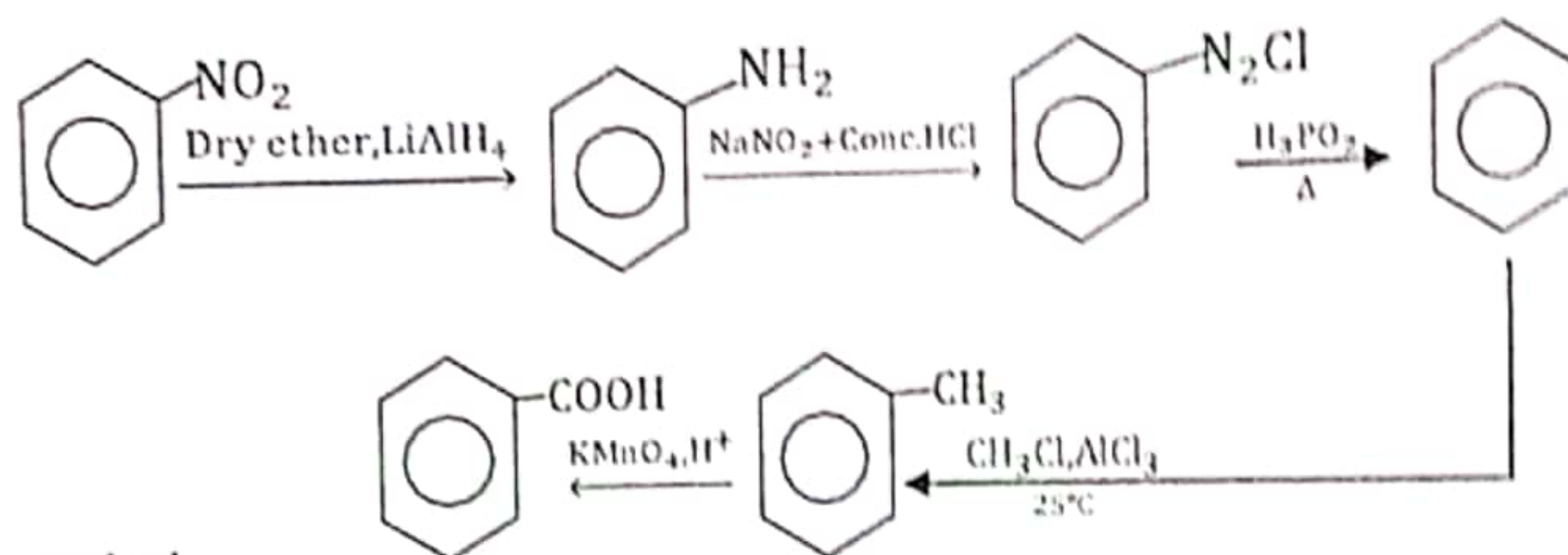
ii)



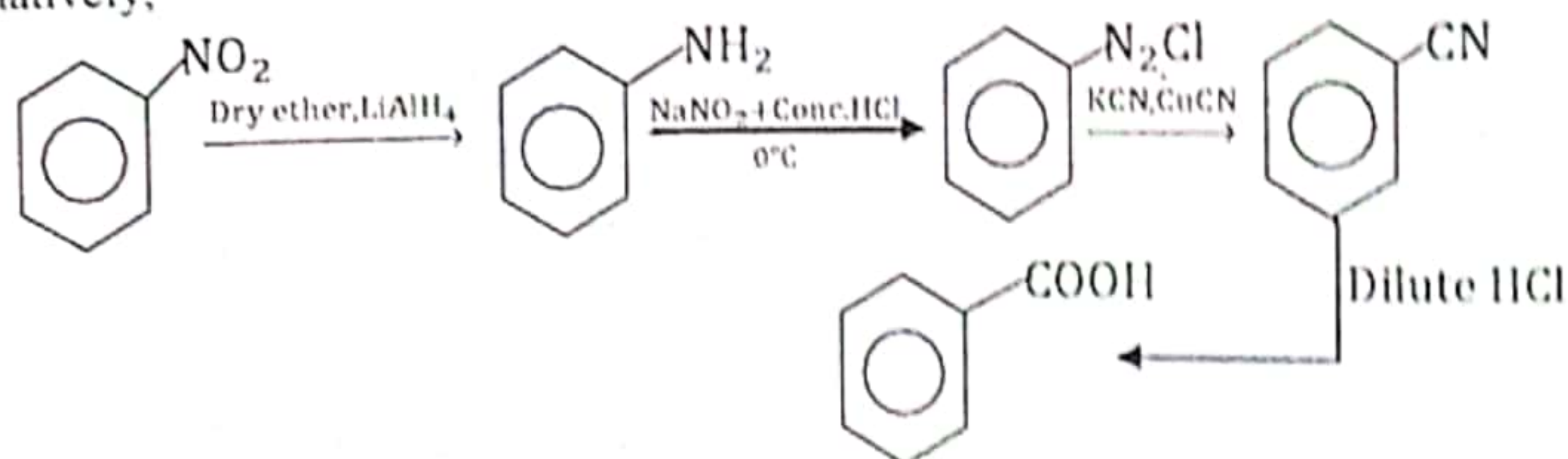
iii)



iv)

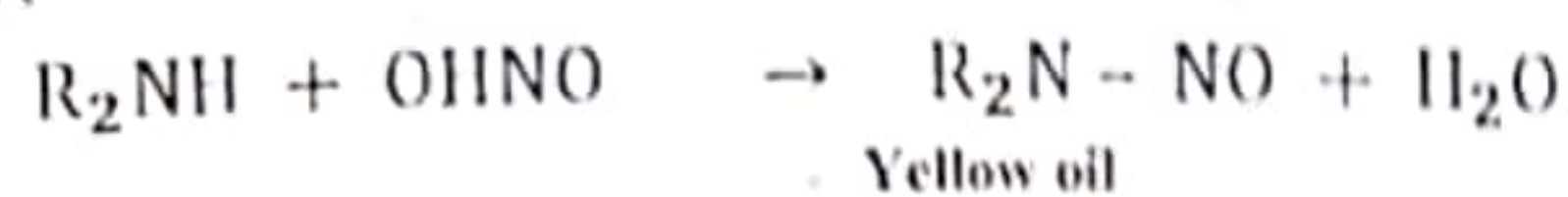


Alternatively;

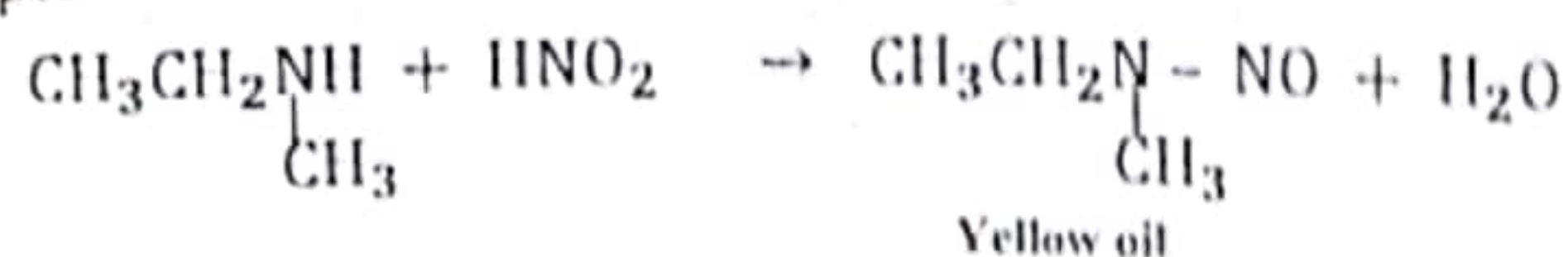


Reaction of secondary amine with nitrous acid

Secondary amine reacts with nitrous acid to form compound which appear as yellow oil. Generally;



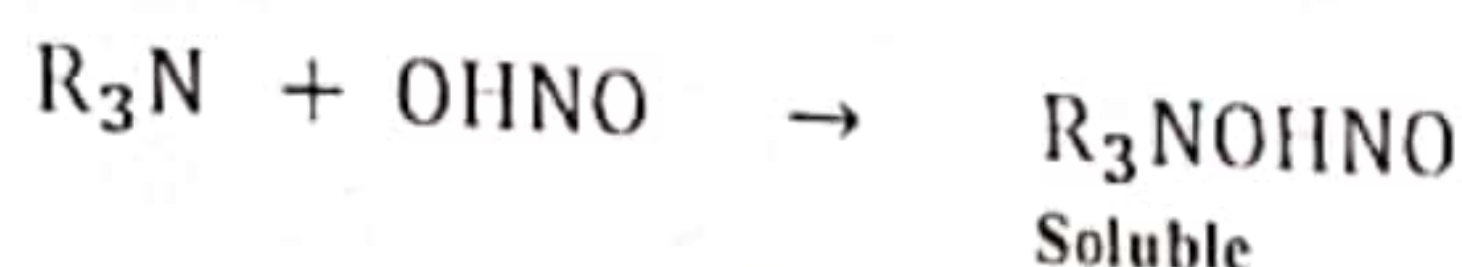
Example



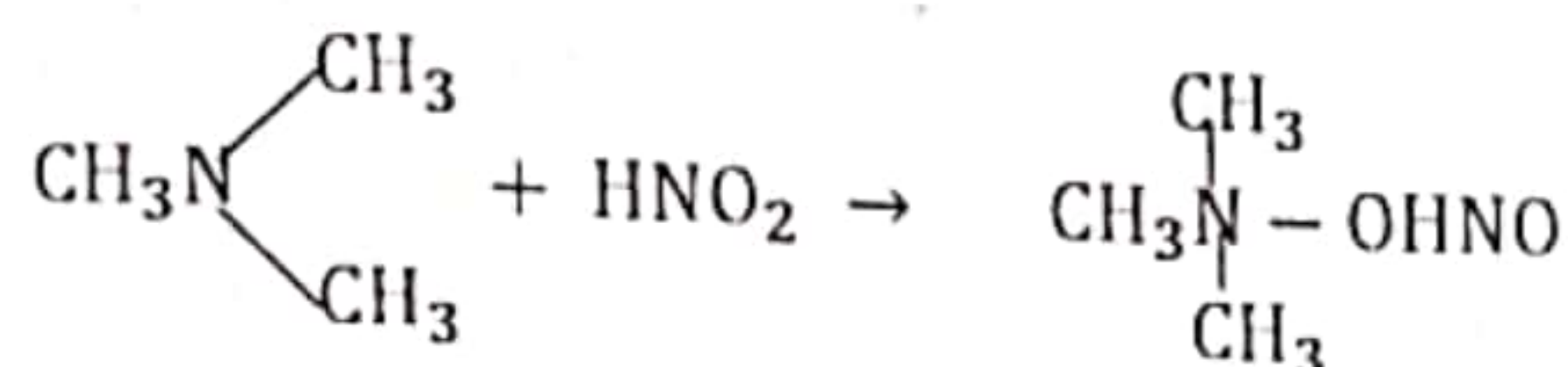
Reaction of tertiary amine with nitrous acid

Tertiary amine reacts with nitrous acid to form soluble compound. (There is no any change which can be observed)

Generally;



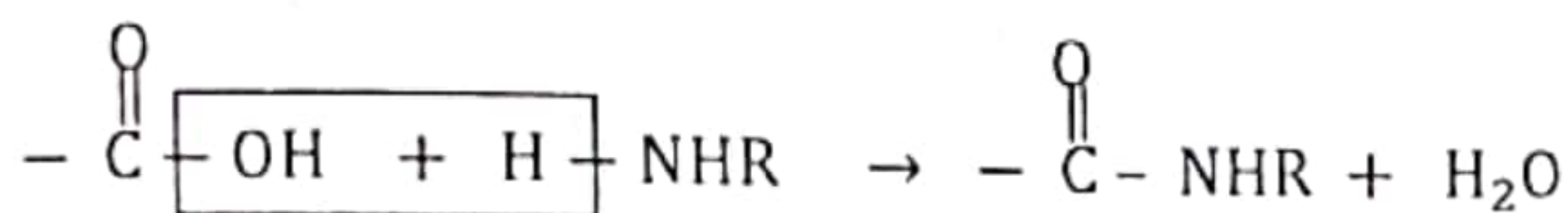
Example,



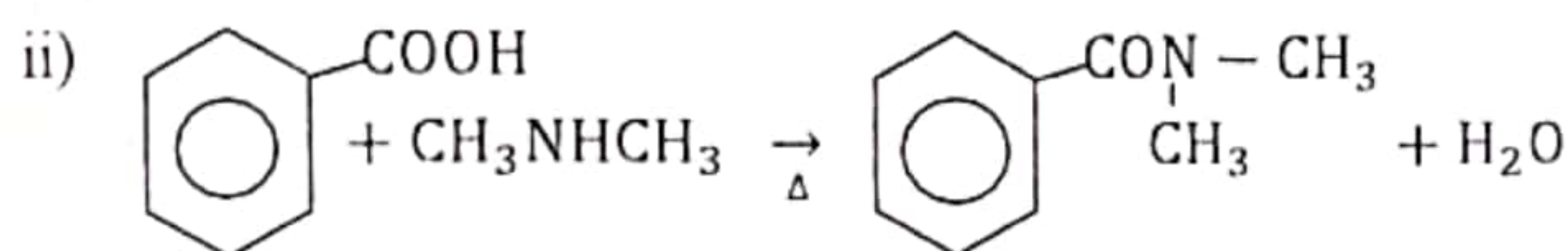
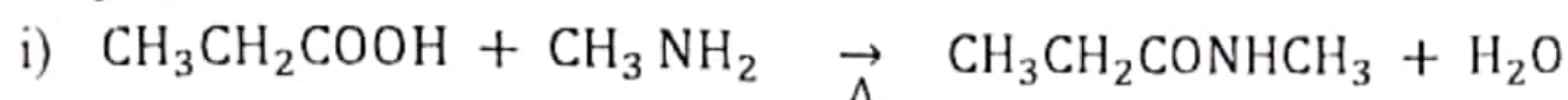
So the reaction between amines and nitrous acid is very useful in distinguishing three classes of amines.

Reaction with carboxylic acid

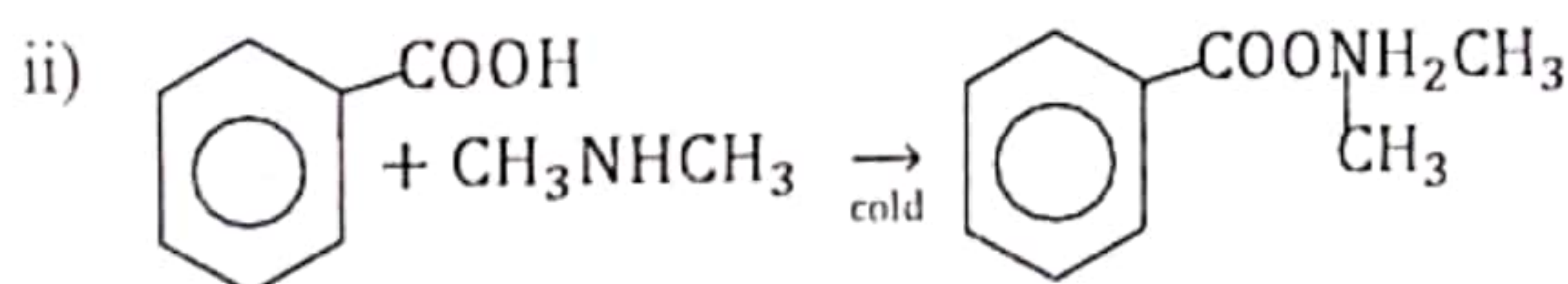
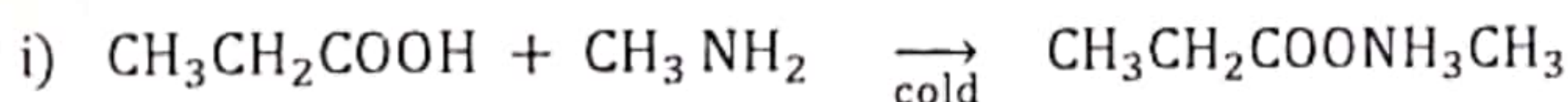
Generally;



Examples:



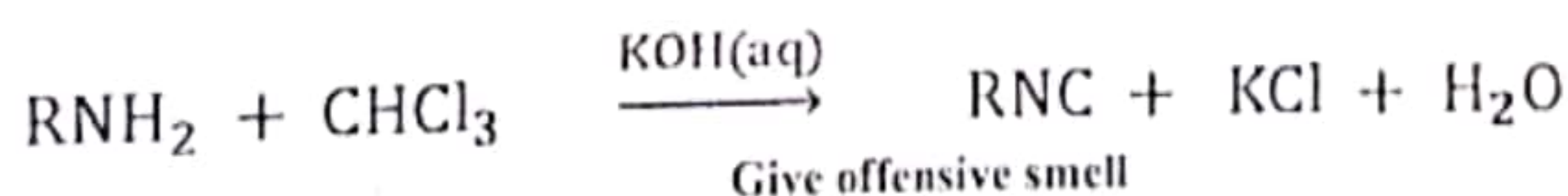
But



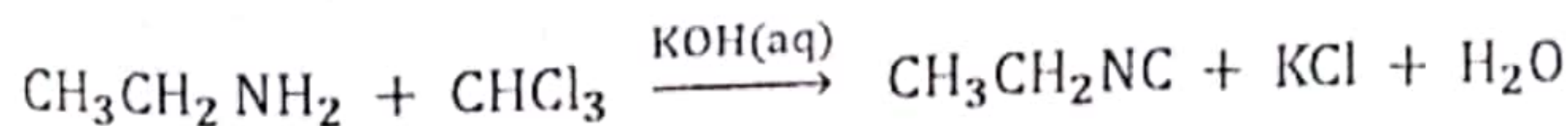
Reaction of Primary amines with chloroform

With chloroform under presence of alkaline solution primary amines give offensive smell of carbylamine.

Generally;



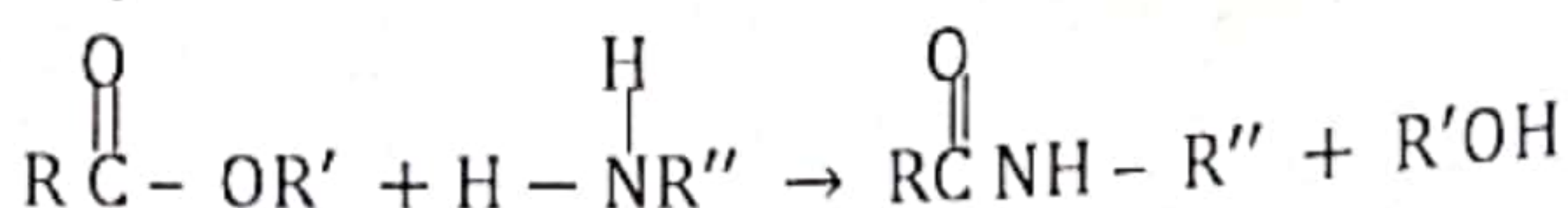
Example



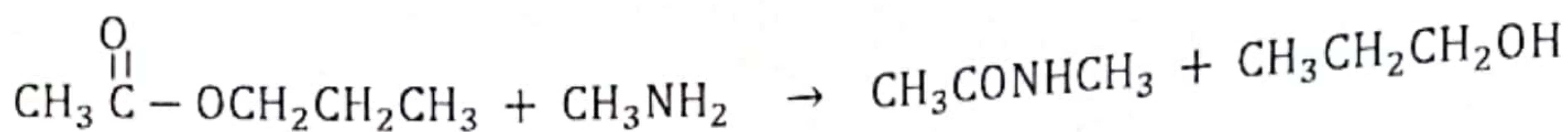
The reaction is very important in distinguishing primary amines from other classes of amines (other classes of amines do not react with chloroform i.e. they do not give offensive smell with alkaline CHCl_3)

Reaction with ester

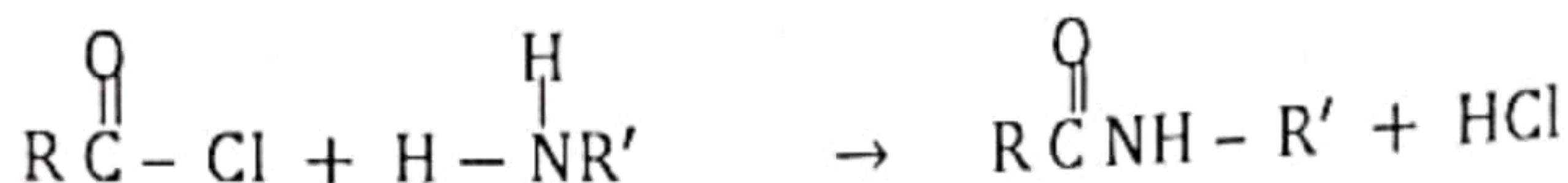
Generally



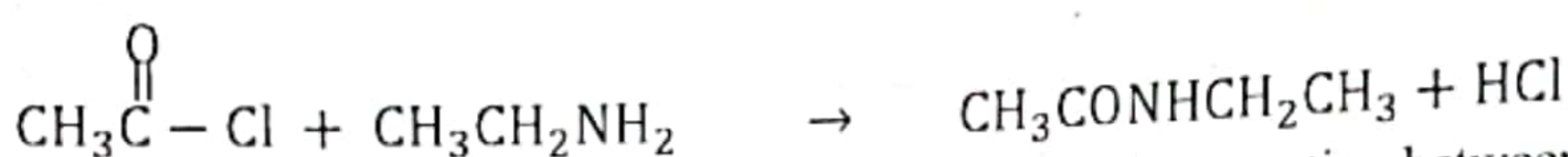
Example

**Reaction with acyl chloride**

Generally;

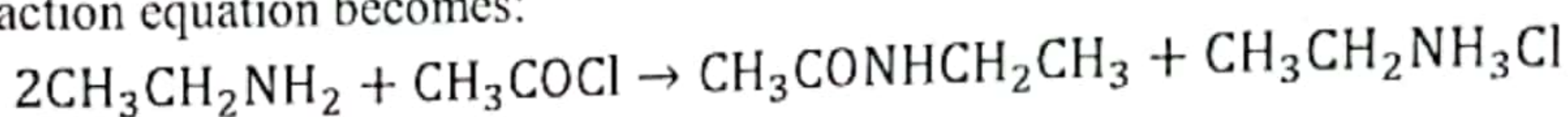


Example,

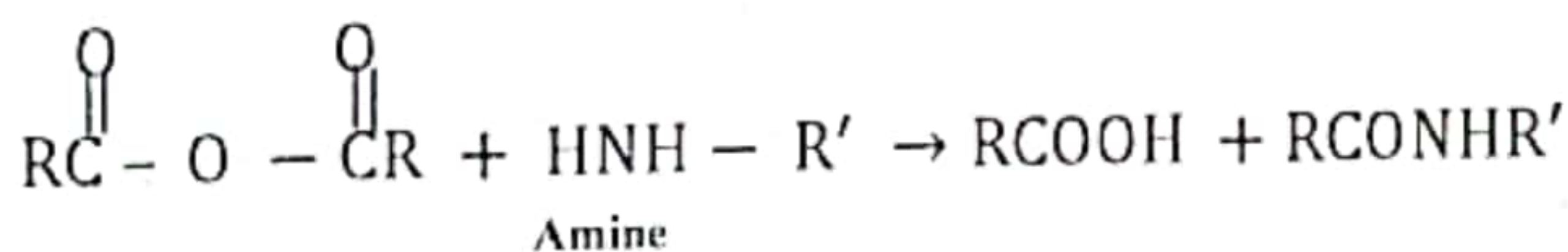


But when amine ($\text{CH}_3\text{CH}_2\text{NH}_2$) is in excess, there is a further reaction between amine and HCl (which is acidic) as per equation; $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$;

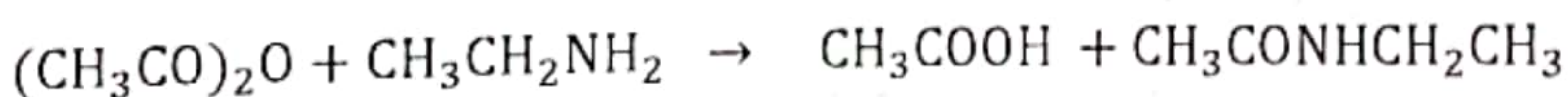
And the overall reaction equation becomes:

**Reaction with acid anhydride**

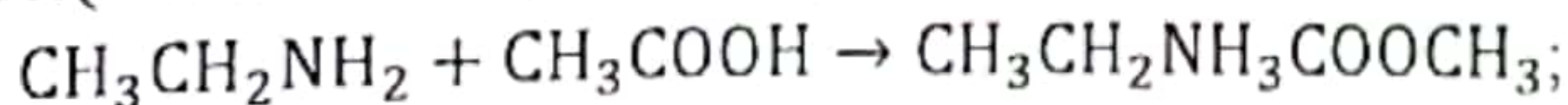
Generally;



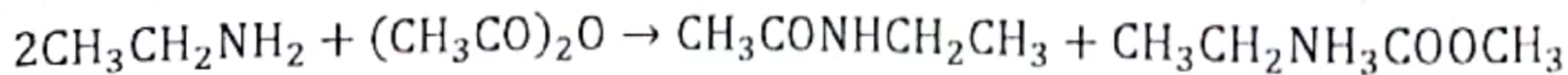
Example,



But if $\text{CH}_3\text{CH}_2\text{NH}_2$ is present in excess, further reaction between $\text{CH}_3\text{CH}_2\text{NH}_2$ and CH_3COOH (which is acidic) occurs as per equation;

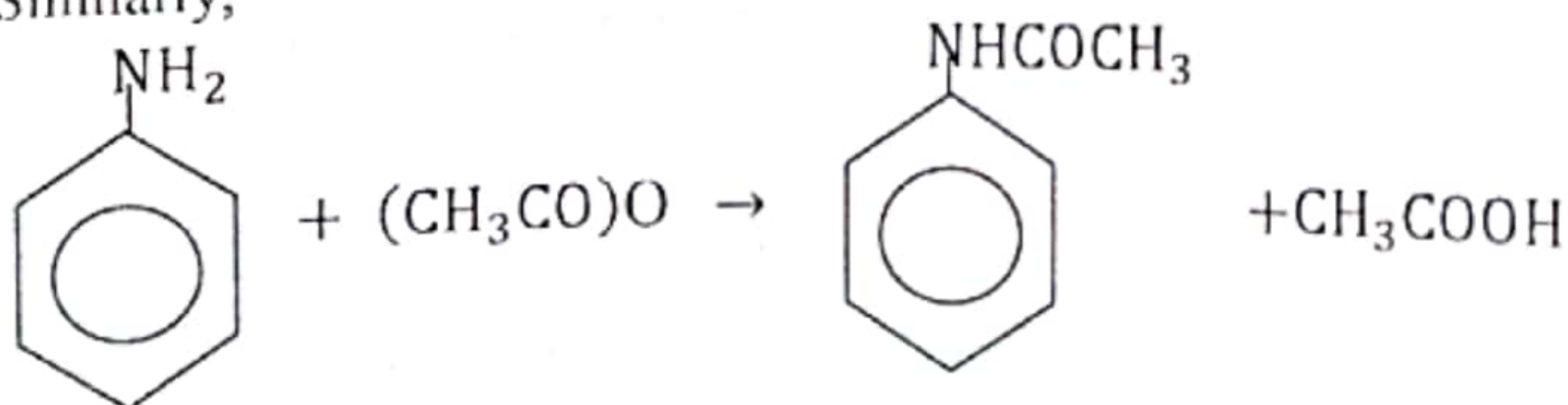


And the overall reaction equation becomes;



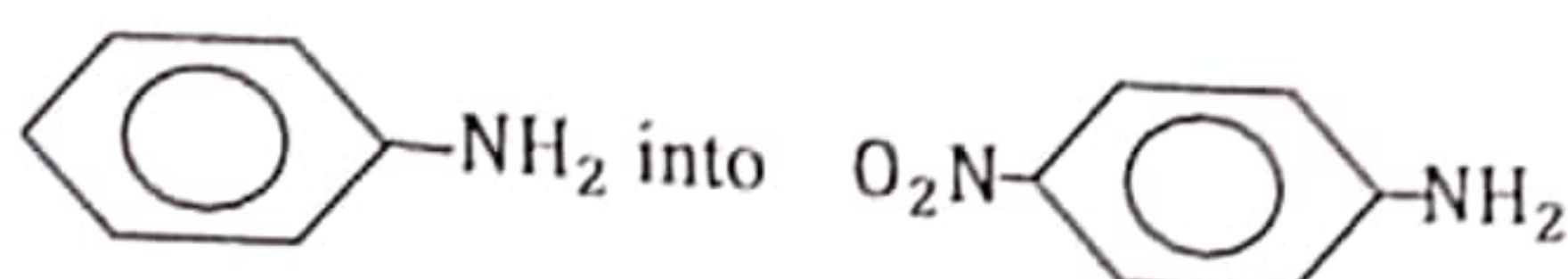
(Don't forget that in presence of heat $\text{CH}_3\text{CH}_2\text{NH}_3\text{COOCH}_3$ undergoes dehydration to give $\text{CH}_3\text{CH}_2\text{NHCOOCH}_3$ and H_2O)

Similarly;

**Interesting!**

The product in the above reaction can be converted back to aniline by concentrated (70%) sulphuric acid thus making acyl group to act as protecting group.

For example ;
Convert

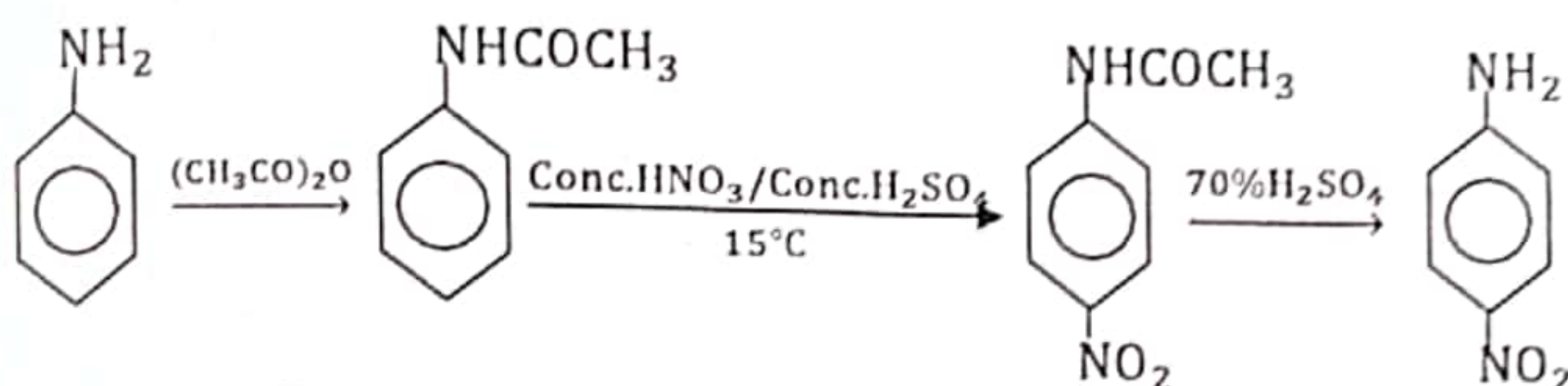


Important tip!

NH_2 group is ortho – para director. Due to its small size NH_2 exerts weak steric hindrance and therefore there is a large percentage of ortho product.

– To prevent formation of ortho product, acylation of aniline should be done first.

So as to introduce a larger sized acyl group which exerts strong steric hindrance to ortho carbon. Here is the solution!



Also note that:

Nitration of  in step 2 in the above conversion requires less temperature (15°C) than

benzene ($50^\circ\text{C} - 55^\circ\text{C}$) because NHCOCH_3 group is an activator (It increases electron density in the benzene ring thus making benzene more reactive towards electrophile, NO_2 group).

Very important to understand that!

Another advantage of introducing the acyl group, it prevents unwanted oxidation of $-\text{NH}_2$ group which is a good reducing agent by concentrated HNO_3 which is a good oxidizing agent.

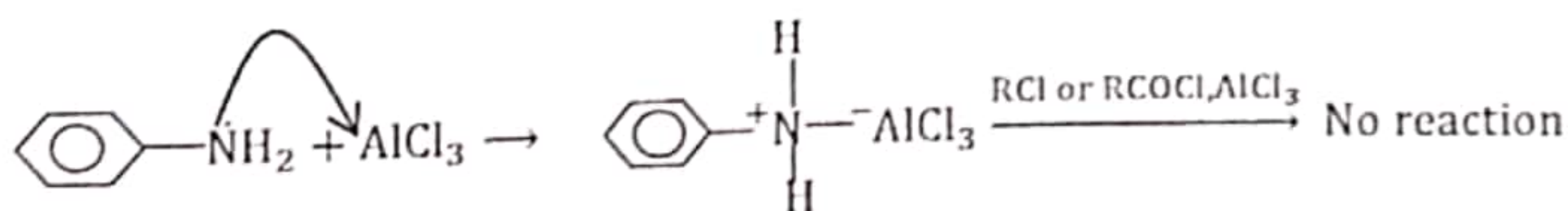
Free radical substitution reaction in aniline

Like any substituted benzene, aniline undergoes free substitution reactions similar to benzene whereby the amino group acts as ortho-para director.

However..!

Friedel-Craft reactions do not occur with aniline because the complex that forms between NH_2 and the AlCl_3 catalyst deactivates the ring towards Friedel-Craft reactions;

That is;



USES OF AMINES

In making dyes

- Primary aromatic amine (anilines) is used as raw material for manufacture of azo dyes. (They react with nitrous acid to form diazonium salt, which can undergo coupling reaction to form azo compound).
- Azo compounds are highly coloured and therefore are widely used in dyeing industries such as methyl orange production

In making drugs and medicines

- Many drugs and medicines are based on amino compounds for examples;
 - Chlorpheniramine is the amine which is used as anti-histamine medicine
 - Heroin is the tertiary amine drug.

Gas treatment

- Amine being basic is widely used industrially to remove acidic gas for example in removing H_2S (and of course CO_2) from natural gas in the refinery process known as **sweetening of natural gas**. (Generally 'sweetening' is the term used for removing acidic or sour gases by amines).

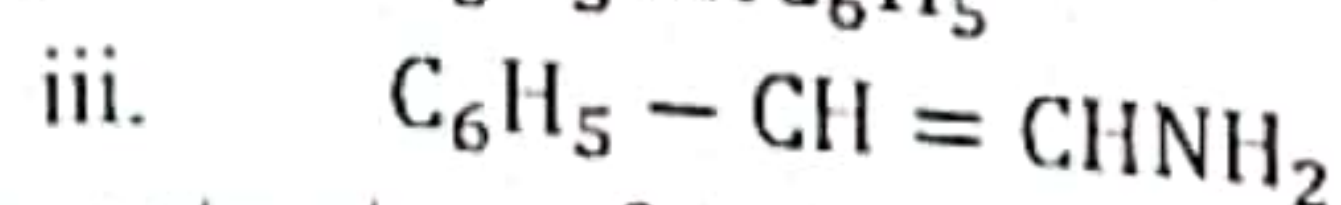
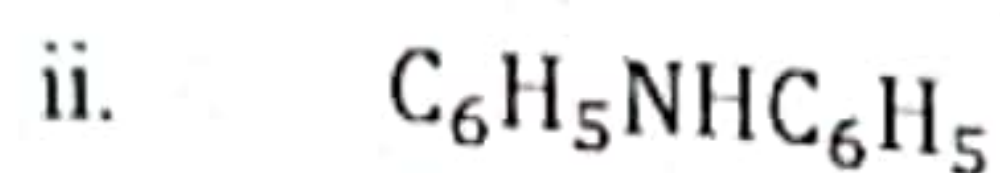
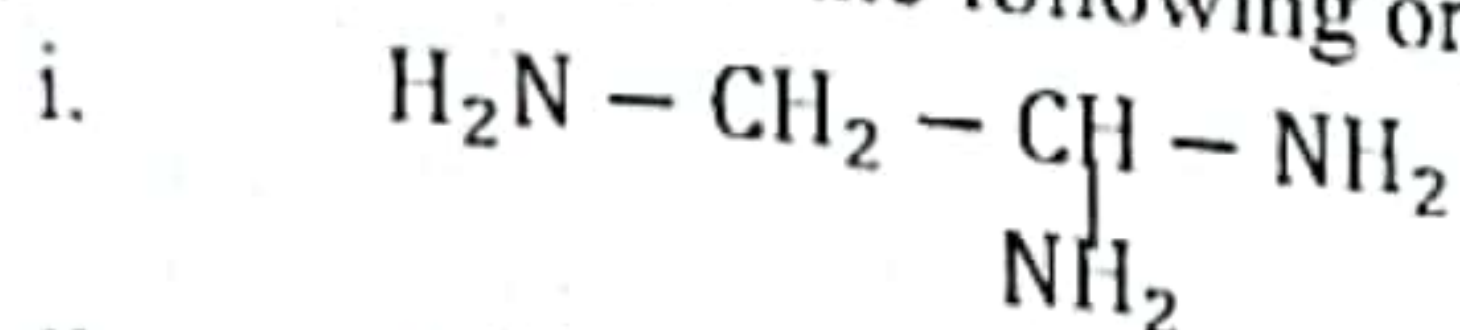
Other uses are:

- As raw material of production of nylon (polymer).
- In making protein which is very important in the biochemistry of the body
- In making quaternary ammonium salts which has various important uses with the principle use of acting as cationic surfactants.

PRACTICE EXERCISE 22

Problem 1

a. Give systematic name of the following organic compounds:



b. Give a structure of an isomer of $\text{CH}_3\text{CH}_2\text{NH}_2$

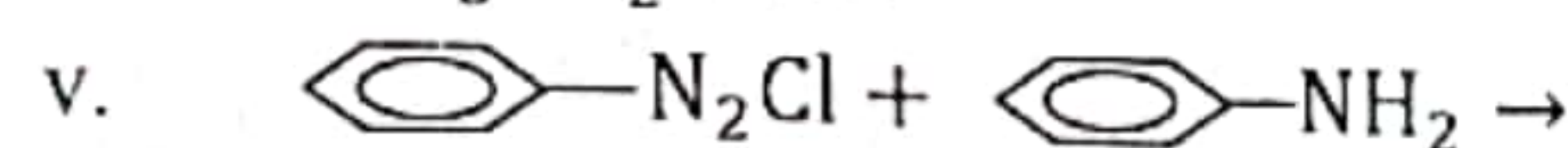
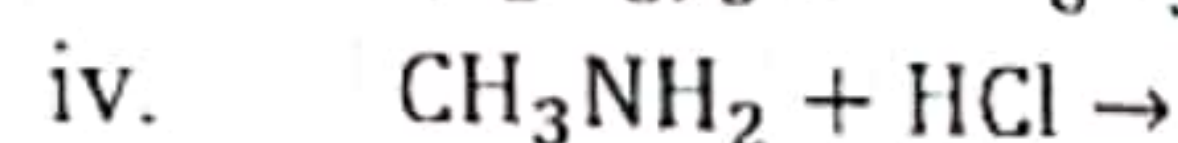
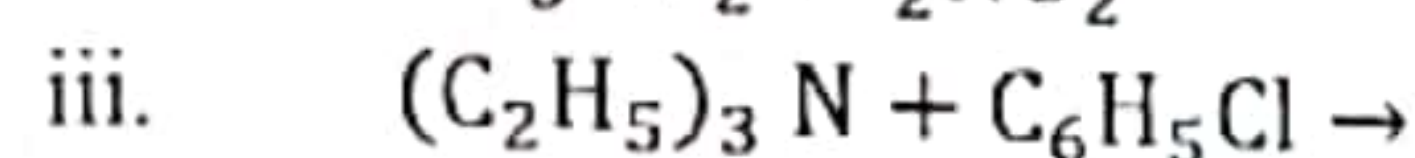
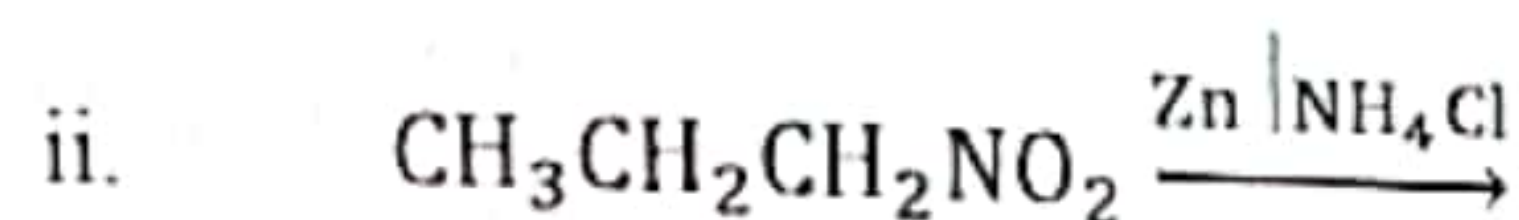
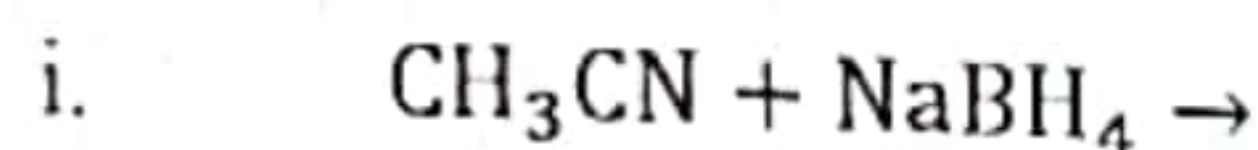
Problem 2

Write an equation to show preparation of ethanamine from:

- Nitrile
- Amide (two ways)
- Nitroalkane

Problem 3

Complete the following reactions:-



Problem 4

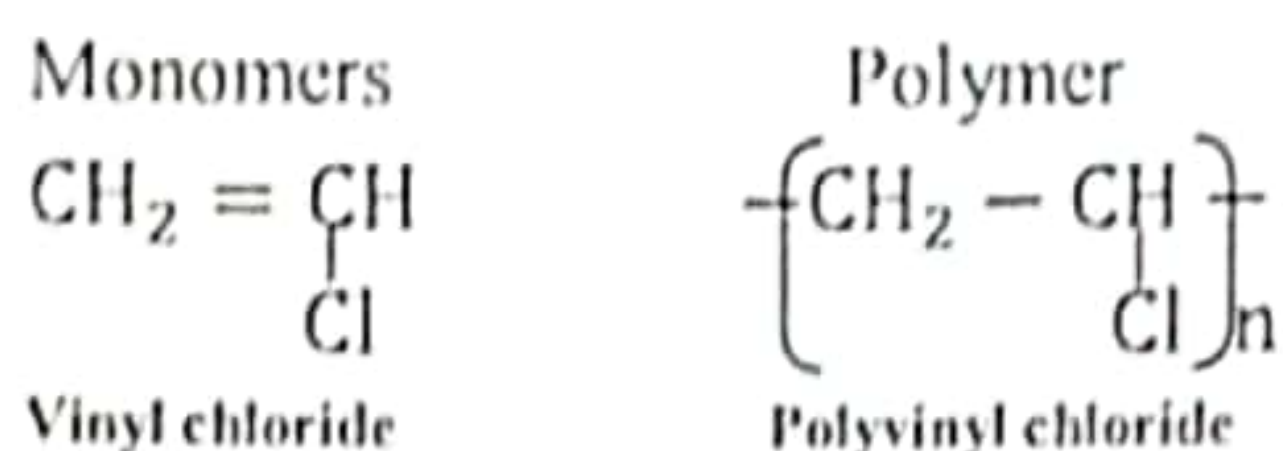
List down at least three uses of amines

Chapter 23 POLYMERS

Polymerisation is the reaction which involves joining up of small molecules so as to form larger molecules.

- **Polymers** are very large molecules which are made up by joining together small molecules called **monomers**.

e.g.



The opposite polymerisation is **depolymerisation** which may be defined as the process where a polymer is broken into its monomer components.

CLASSIFICATION OF POLYMERS BASED ON SOURCE OF AVAILABILITY

Polymers can be classified based on the basis of their source of availability as

- Natural polymers
- Semi-synthetic polymers and
- Synthetic polymers

Natural polymers

Natural polymers are polymers occurring in nature in plants and animals.

- Examples of natural polymers are starch, cellulose, protein, silk, wool and natural rubber.

Polymers which include various biomolecules such as protein and carbohydrates are known as **biopolymers**.

Semi-synthetic polymers

Semi-synthetic polymers are polymers which are derived from natural occurring polymers by chemical modifications.

- A good example of this is **vulcanised rubber** which is used in making tyres.

Synthetic polymers

Synthetic polymers are polymers which are made by man.

- Examples of synthetic polymers are fibers, synthetic rubbers and PVC (Polyvinyl chloride)

CLASSIFICATION OF POLYMERS BASED ON MODE OF POLYMERISATION

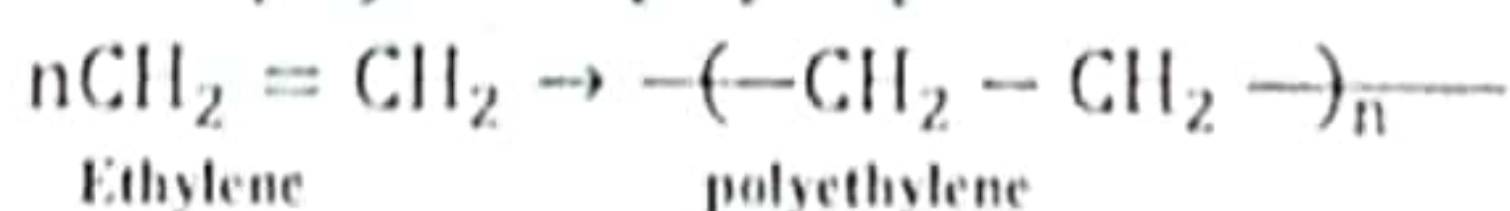
According to their mode of polymerisation, polymers can be classified as:

- Homopolymers and Copolymers
- Addition and condensation polymer

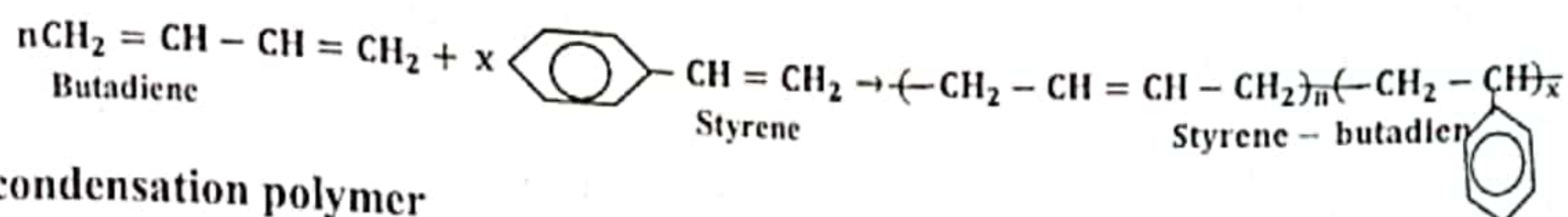
Homopolymers and Copolymers

Homopolymer is a polymer which is formed from only one kind of monomer. It is also known as **simple polymer**

- A good example of homopolymer is **polyethylene**.

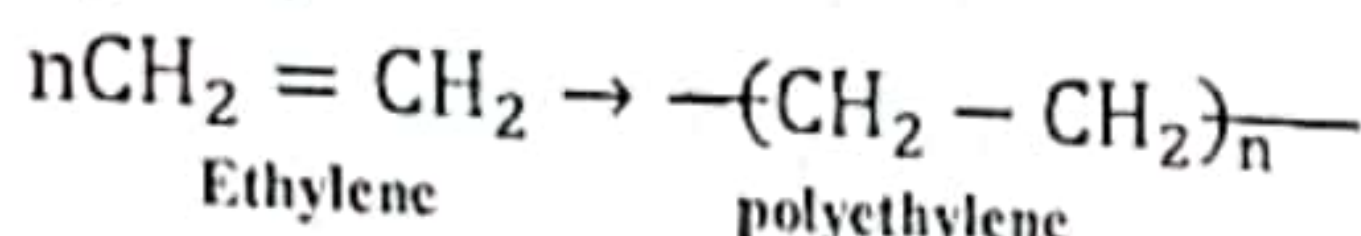


- A good example of copolymer is poly(styrene-butadiene) which is formed from styrene and butadiene

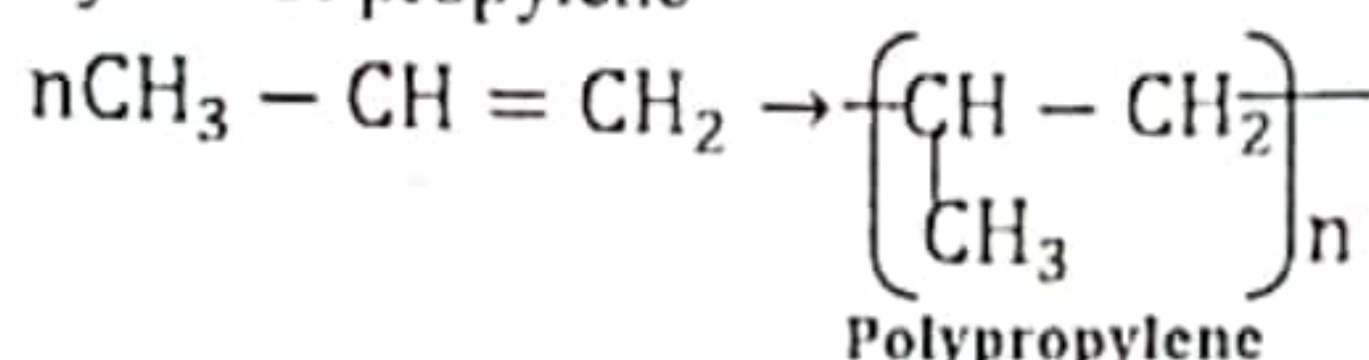


Addition polymer is formed by combining unsaturated monomers through addition reaction.

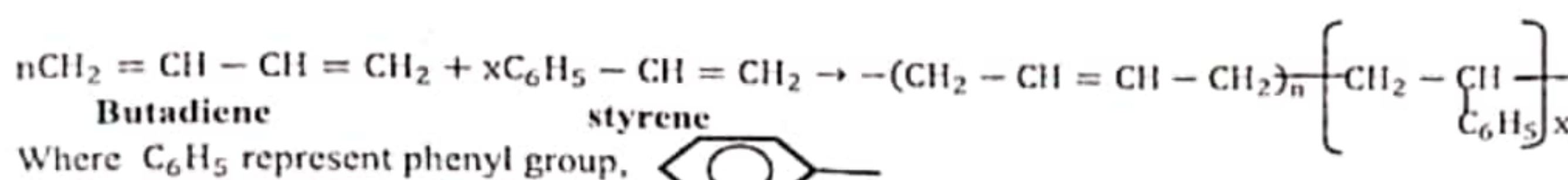
i. Polyethylene (or polyethene) which is formed from addition polymerisation of ethene (common name ethylene)



ii. Polypropylene which is an addition polymer of propylene

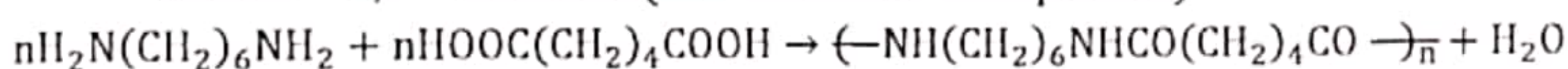


iii. Styrene-butadiene which is formed from addition polymerisation between styrene and butadiene.



Condensation polymer is formed by combination of two or more monomers accompanied with evolution of small molecule.

- Examples of condensation polymers is nylon-66 which is formed from condensation of hexane - 1,6 - diamine (Common name is hexamethylene diamine) and hexane - 1,6 - dioic acid (common name is adipic acid)



According to their mode of linking (arranging) monomers;

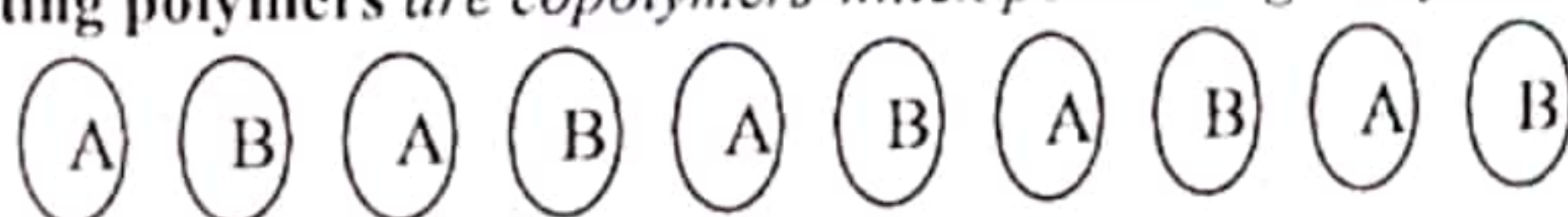
Polymers can be classified as:

- Alternating, block and random polymers
- Linear, minor cross-linked and massively cross-linked polymer

Alternating, block and random polymers

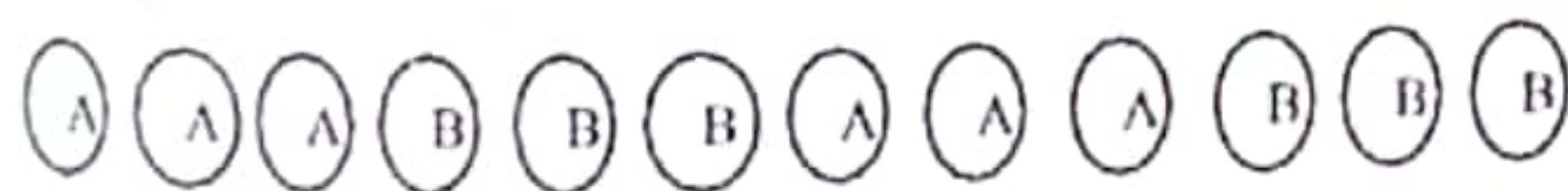
i. Alternating polymers

Alternating polymers are copolymers which possess regularly alternating monomer residues.



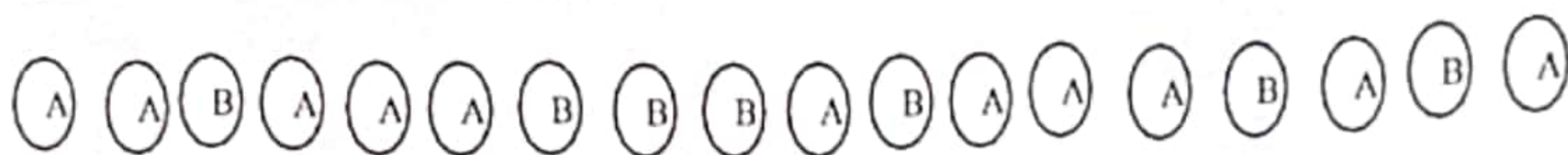
ii. Block polymers

ii. **Block polymers**
Block polymers are copolymers which have two or more homopolymer sub-units linked by covalent bonds.



iii. Random polymers

Random polymers are copolymers which are comprised of two or more different monomer units attached in a random order.



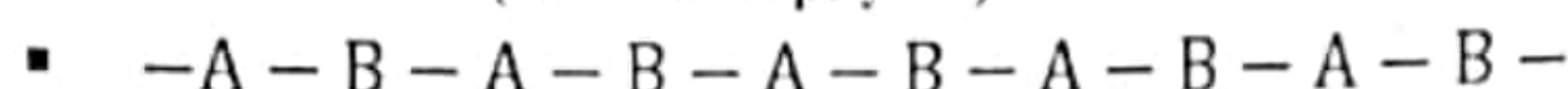
Linear, minor cross-linked and massively cross-linked polymer

Linear polymer

- This has no cross linkage at all. Its straight chain polymer.



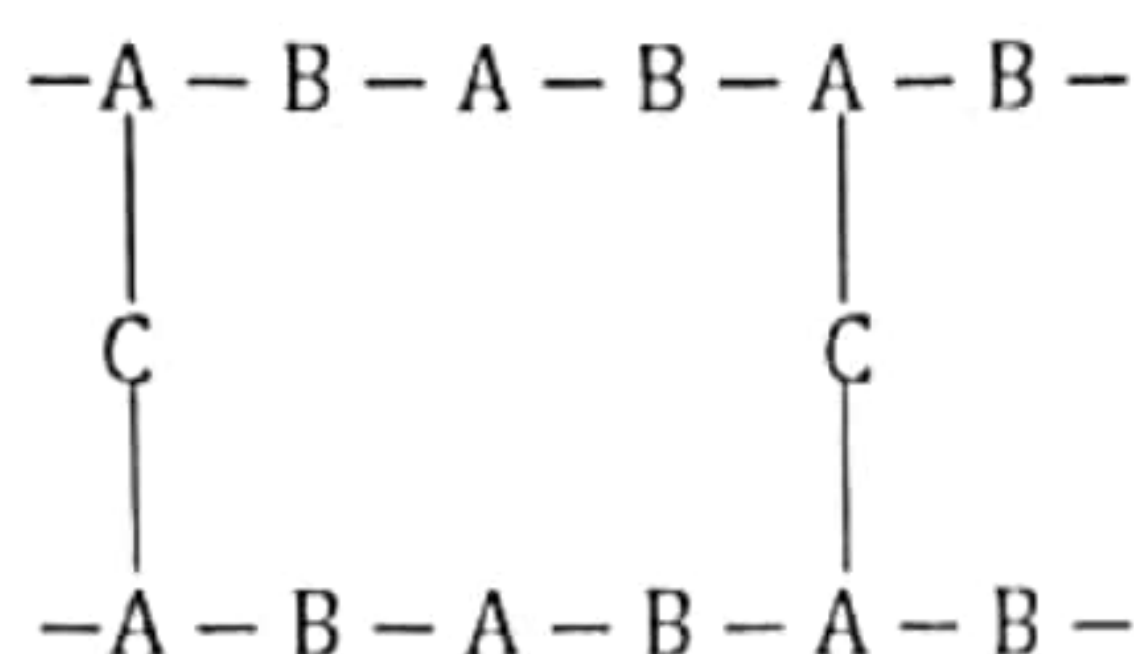
(Linear homopolymer)



(Linear alternating copolymer)

Minor cross-linked polymer

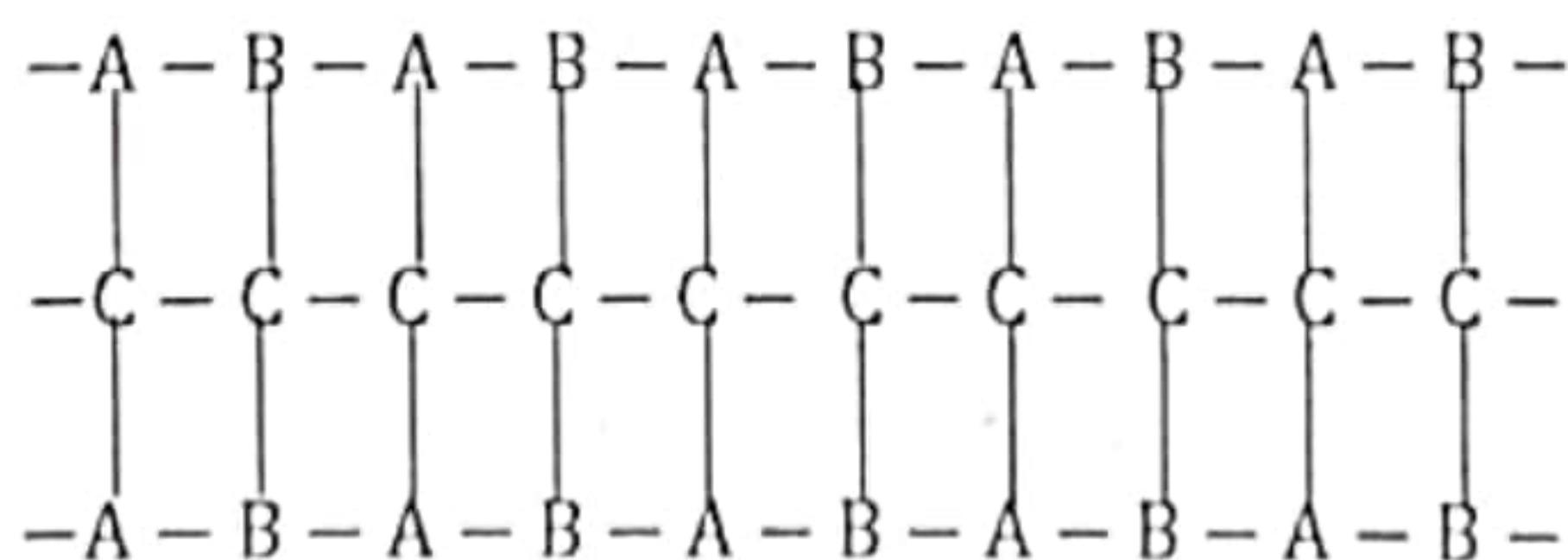
- These have few cross-links.



Where **cross-link** is the bond that joins two separated polymer chains together. (In the above example, cross link is A – C bond).

Massively cross-linked polymer

- These have many cross –links.



CLASSIFICATION OF POLYMERS BASED ON INTERMOLECULAR FORCES

According to the strength of their intermolecular forces of attraction, polymers can be classified as

- Elastomers
- Fibers
- Thermoplastics and
- Thermosetting polymers

Elastomers

Elastomers are polymers in which the polymer chains are held by weakest intermolecular forces of attraction.

- These forces are so weak that they allow polymers to be stretched.
- A few cross links may be introduced between the chains to help the polymer to retract to its original position after the force is released. A good example of this is **vulcanised rubber**.

Properties of elastomers

- i. They consist of very long polymer molecules.
- ii. They have few cross linking
- iii. Can be melted without decomposition.
- iv. They show elasticity at room temperature.

Fibers

Fibers are polymers with high tensile strength and high modulus due to presence of strong intermolecular forces (like hydrogen bonding existing in polyamides).

- These strong forces also lead to close packing of chains and therefore impart crystalline nature to the polymer. These are used for making fibers.
- Examples of polymers falling to this category are nylon and terylene.

Thermoplastics

Thermoplastics are polymer materials which soften when heated without decomposition and become hard when cooled.

- Are polymers whose strength of their intermolecular forces of attraction lies between those of elastomers and fibers.
- The polymer chain has no cross links and therefore thermoplastics can be moulded on heating.
- Examples of thermoplastics are polyethene (also known polyethylene) and polystyrene.

Properties of thermoplastic polymers

- i. Their molecules are linear
- ii. They are soft at room temperature
- iii. They have low melting and boiling points because they have weak Van – der – Waal forces of attraction or hydrogen bonding.
- iv. They have high solubility in organic solvents.
- v. Can be remoulded.

Thermosetting polymers

Thermosetting polymers are polymer materials which are hard and soften when heated with decomposition. Once hardened, they cannot be softened by re-heating.

- Are polymers made from relatively low molecular mass semi-fluid polymers which when heated in a mould, form an insoluble mass which is infusible.
- They form insoluble mass which is infusible because they have massive cross-links between different polymer chains forming three dimensional networks of bonds.

An example of thermosetting polymer is **bakelite plastic** which is formed when phenol reacts with formaldehyde in the presence of either an acid or a base.

- The reaction leads to network polymers because the molecule can react at both ortho and para positions.
- Another example of thermosetting polymer is **melamine**.

Properties of thermosetting polymers

- i. They have cross linked molecules.
- ii. They are hard and brittle hence they have three dimension giant structures.
- iii. They have high melting point
- iv. They are insoluble in organic solvent.
- v. Cannot be melted without decomposition.

FACTORS AFFECTING PHYSICAL PROPERTIES OF POLYMERS

- (i) **Chain length**
Generally, the longer the chains the stronger the polymer
- (ii) **Side groups**
Polar side group give stronger attraction between polymer chains making the polymer stronger.
- (iii) **Branching**
Straight (unbranched) chains give stronger attraction between polymer chains and hence the polymer becomes stronger.
- (iv) **Cross –linking**
If polymer chains are linked together extensively by covalent bonds, the polymer becomes harder and more difficult to melt.

SYNTHESIS OF POLYMERS

Polymers can be synthesized by the following ways:

- Addition polymerisation
- Condensation polymerisation

Addition polymerisation

This is the polymerisation which is done by combining unsaturated monomers through addition reaction.

- Addition polymerisations are commonly undergone by alkenes and hence the term **polyalkenes** for addition polymers.
- Addition polymerisation is also known as **polyaddition**.

Addition polymerisation occurs in such a way that unsaturated monomer molecules add to an active site (radical or ion) on growing polymer one at a time hence the term **chain-growth polymerisation** (or **simply chain polymerisation**) for addition polymers.

- Most of addition polymers are **plastics**.

By definition **plastics** are synthetic polymers that can be shaped by heat and pressure.

Addition polymerisation can further be divided into two types:

- Free radical addition polymerisation
- Ionic addition polymerisation

Free radical addition polymerisation

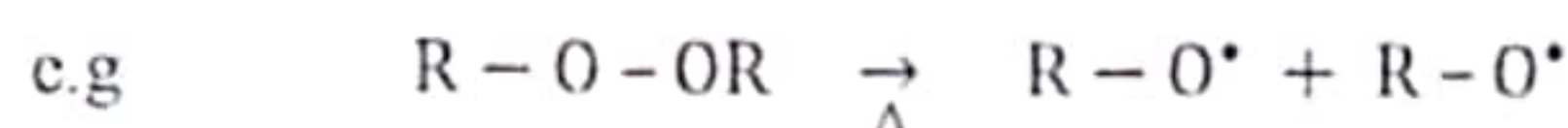
This is the addition polymerisation which takes place under presence of free radical initiator.

It undergo in three steps

- i. Initiation step
- ii. Propagation step
- iii. Termination step

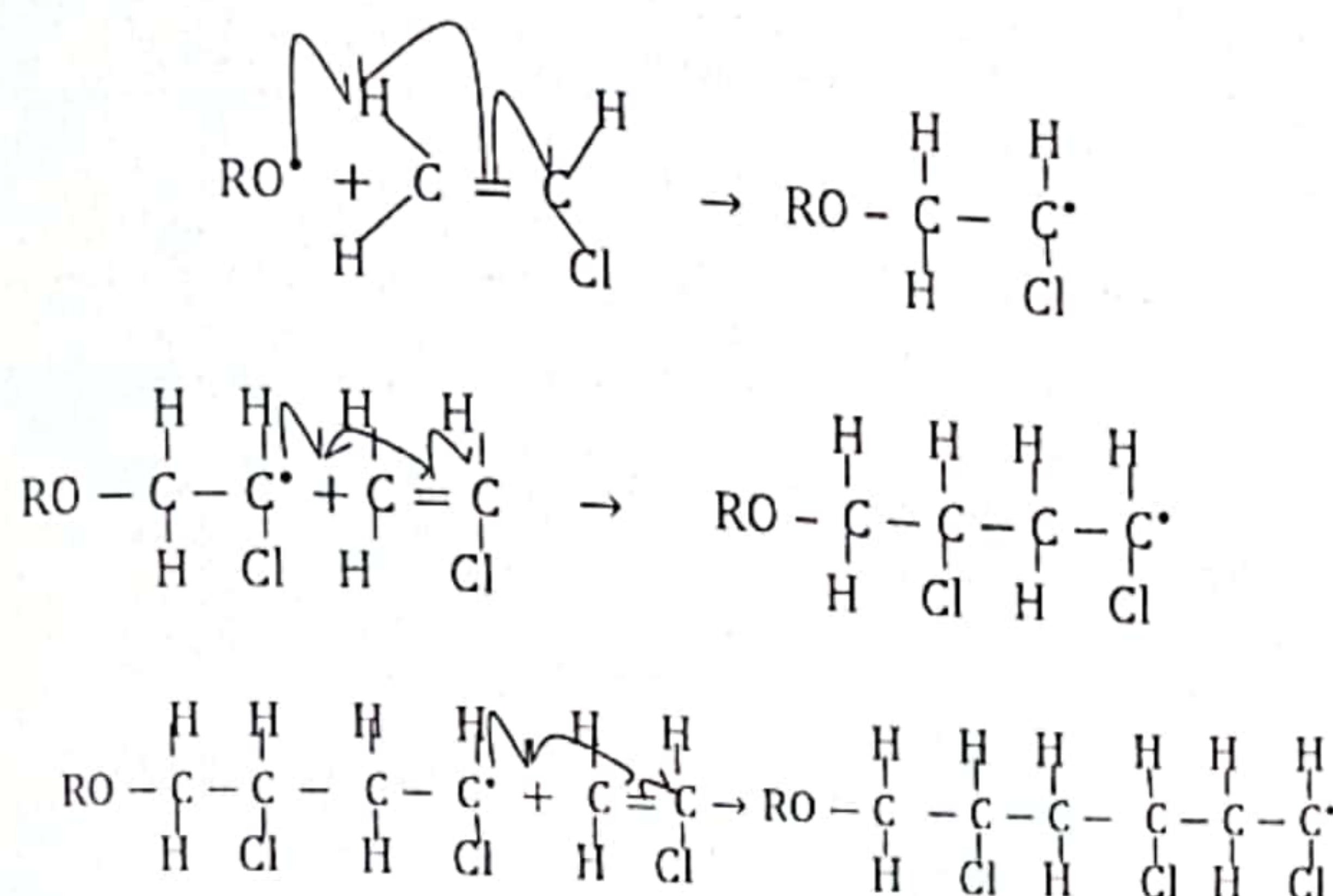
i. Initiation step

This involves formation of free radical. When organic peroxide is heated to very high temperature free radicals are formed.



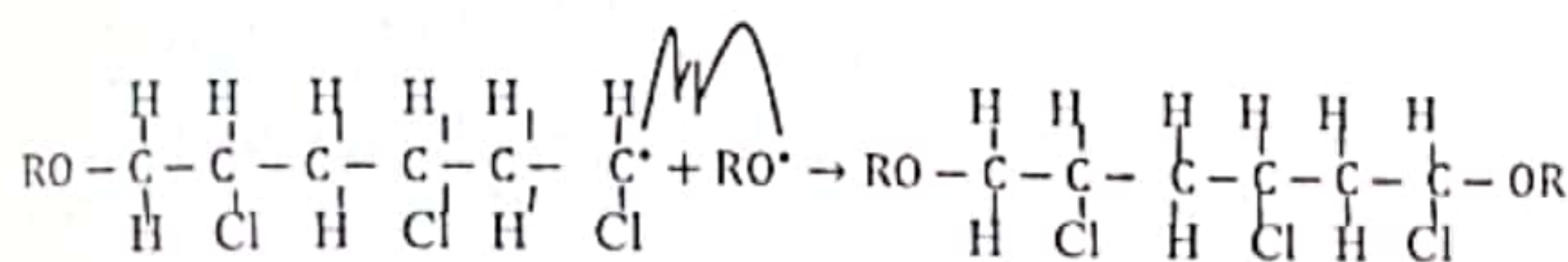
ii. Propagation step

This involves the combination between free radical and molecule, in this case unsaturated monomers.
i.e

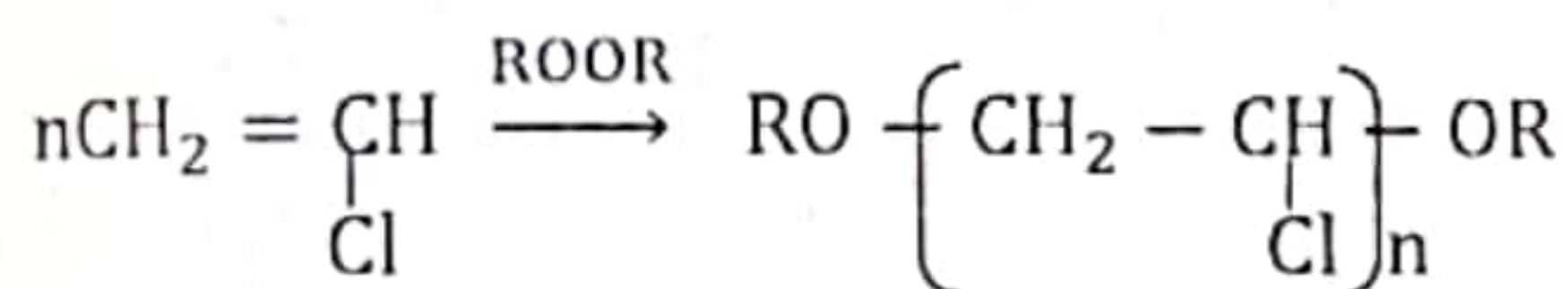


iii. Termination step

This involves combining of free radicals.i.e



The overall reaction equation for the polymerisation is;



Understand this!

When concentration of free radicals is high termination step will be reached earlier and hence the polymer will be shorter and vice versa.

Ionic additon polymerisation

This the type of polymerisation which take place under presence of acid or basic initiator

It can further divided into two types:

- Anionic addition polymerisation
- Cationic addition polymerisation

Anionic addition polymerisation

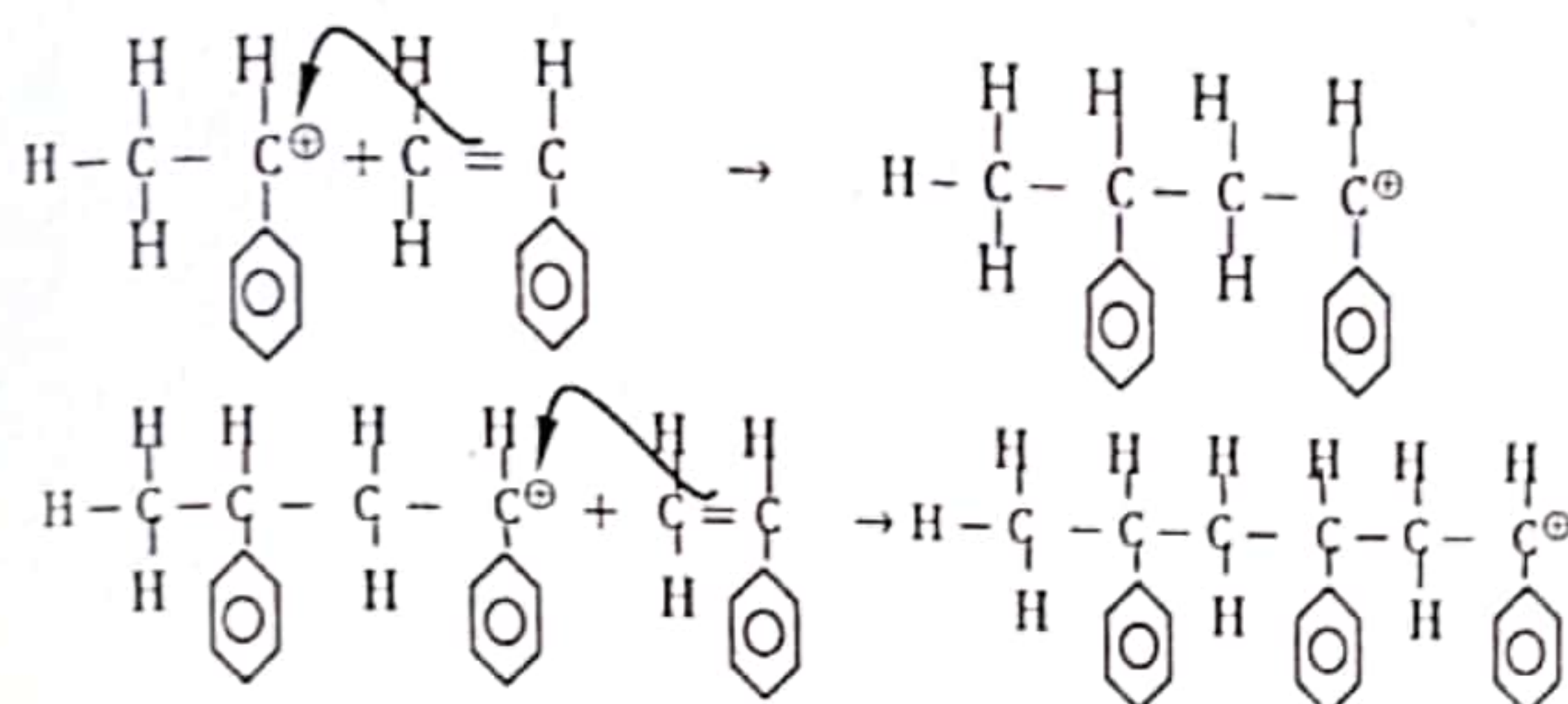
This is the polymerisation which takes place under presence of basic initiator. Example: NH_2^- , OH^- , RO^-

It also undergoes in three steps

- Initiation step
- Propagation step
- Termination step

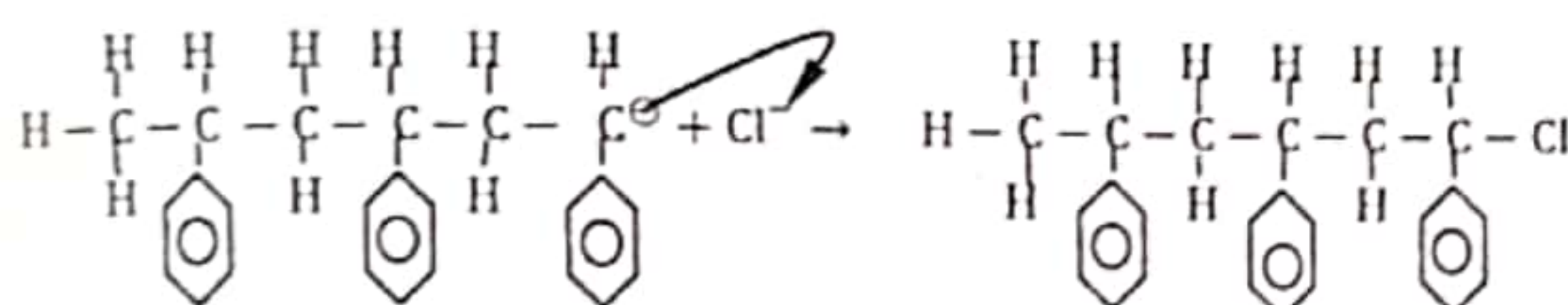
ii) Propagation step

This involves combination of carbenium ion and unsaturated monomers.

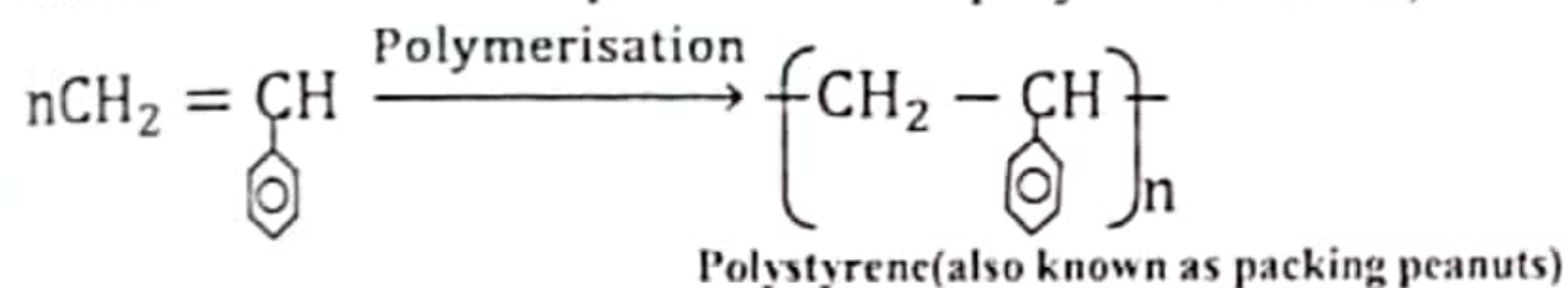


iii) Termination step

This involves the combination between larger carbenium ion and negatively charged ion e.g Cl^- . i.e

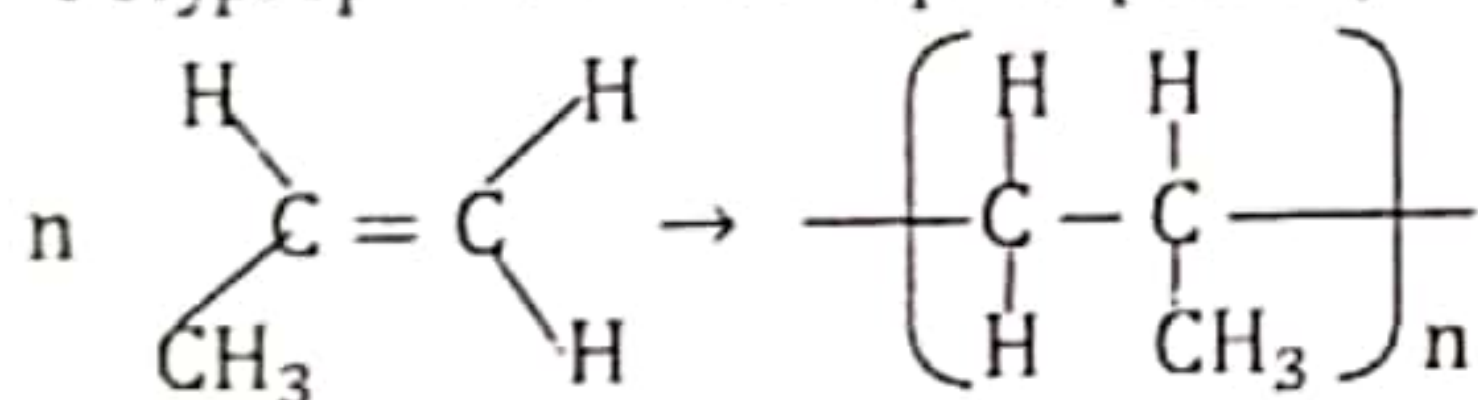


The overall reaction equation for the polymerisation is;

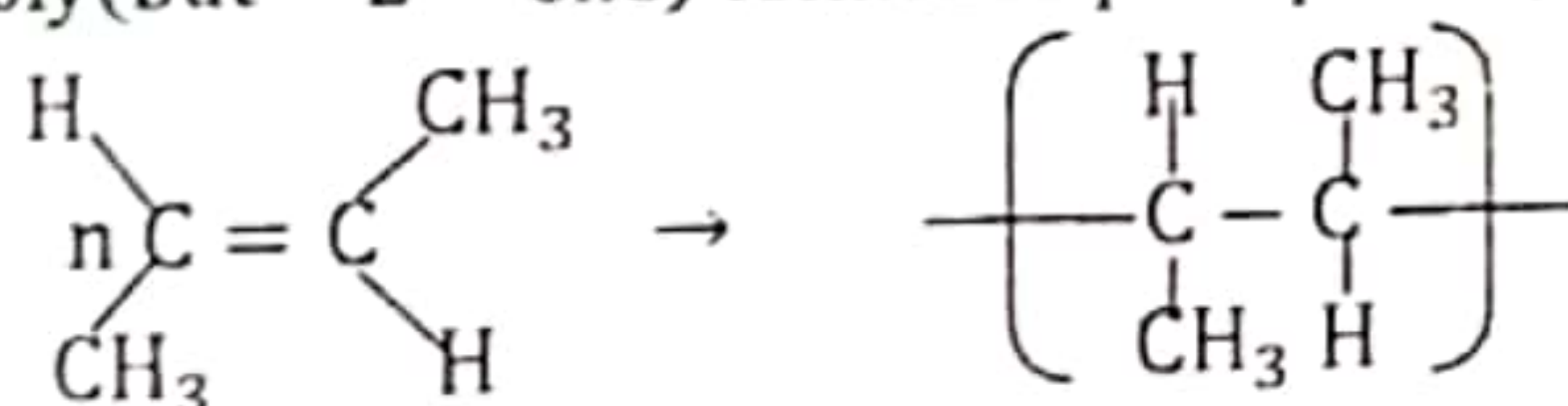


Other examples of additional of polymers

(i) Polypropene formed as per equation;



(ii) poly(but - 2 - ene) formed as per equation;



Conditions which favour additional polymerisation

Condition which favours polymerisation of unsaturated organic compound can be deduced from the fact that:

- The reaction is exothermic. This is simply because the reaction involves breaking of π -bonds only, and many σ -bonds are made. (Remember that π -bonds are less stable than σ -bonds and increase in stability means thermally exothermic process)
- The reaction involves a reduction in the total number of moles. (Also remember that ; polymerisation is the association process which combine small molecules into larger molecule).

How above two facts will help us to deduce conditions favouring addition polymerisation?

This is simply done by applying Le-chatelier's principle as follows:-

- Since the reaction is exothermic high percentage yield of the polymer is obtained at low temperature. But at low temperature the best yield is obtained at very slow rate and hence catalyst is required to obtain the best yield at reasonable rate.

- Since the reaction involve reduction of number of moles high pressure is required to get high percentage yield of the polymer.

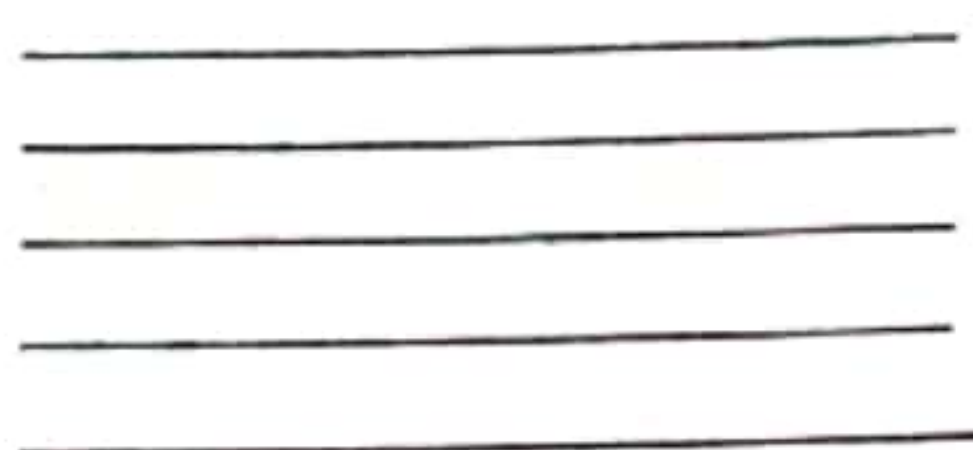
In just single sentence!

Addition polymerisation reactions are carried out at **high pressure** in the presence of a **suitable catalyst**.

Properties of addition polymers

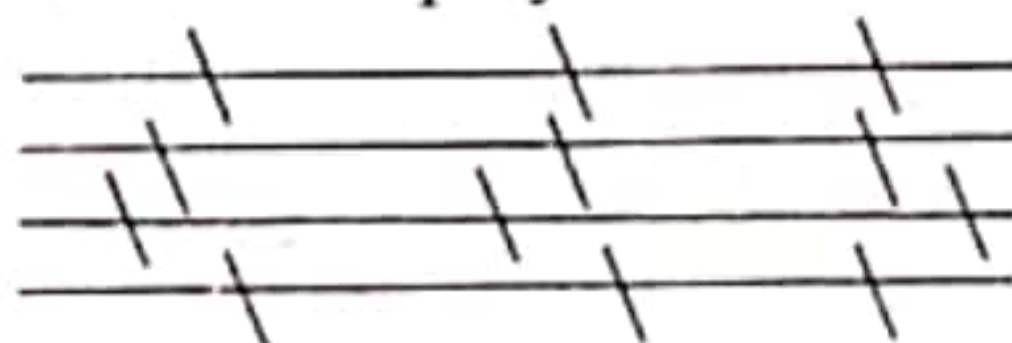
(i) Melting and boiling point

- Oftenly, addition polymers have relatively high melting and boiling point because their chains are often long resulting the strong Van-der-waals forces of attraction between the chains.
- Addition polymers also have significant softness because their chains are not rigidly held in place by each other.
- On another hand, polymers with very few branches (or no branches at all) are very compact (closely packed) and there fore the chains can pack together very efficiently.
- Due to this good packing of chains in space, the Van-der-waals forces between the chains are strong and hence these polymers tend to be harder polymer with high melting and boiling point.



Unbranched polymer chains

- The situation is opposite to polymers which are highly brached.
- These polymers are not closely packed thus making the Van-der-waal's forces between chains weaker and as result the polymers become softer with low melting and boiling point



(ii) Solubility

- Since their chains are non-polar, addition polymers are insoluble in water which is polar solvent.
- Since the intermoleclar force between the molecules are strong and the chains are often tangled, addition polymers are generally insoluble in non-polar solvent as well.

(iii) Density

To a large extent, density of addition polymers depends on the nature and extent of the branching on the chain.

- Polymers with unbranched chains have very high density because they are very compact and therefore they occupy small volume.
- Polymers with branched chains are not closely packed and therefore occupy large volume and hence they have low density.

(iv) Reactivity

Because addition polymers (polyalkenes) are commonly very long saturated hydrocarbon containging non- polar C – C bond they are general very unreactive.

- Little reactivity of addition polymers, explains why they have very large use as inert material such as in packaging, in insulators and in making containers.

- However their little reactivity means they are **non-biodegradable** (they are not decomposed easily by living organisms) and eventually have a very long life time. This makes them to constitute an environmental hazard because their persistent nature makes it difficult to dispose off.

Why is the unreactivity of plastics (addition polymers), has both advantage and disadvantage?

- Their unreactivity makes plastic durable and able to safely contain and protect many substances. This is an advantage.
- However, it also means that they persist in the environment for long time and therefore become serious environmental pollutants. This is a disadvantage.

Uses of addition polymer

Polyethylene is used in:

- Plastic bags
- Insulation for wires

- Squeeze bottles
- Crates

Polypropylene is used in:

- Fibres
- Indoor-outdoor carpets

- Bottles

Polystyrene is used in:

- Styrofoam
- Cheap household goods (like window frames)
- Cheap molded objects

Polyvinyl chloride (PVC) is used in:

- Synthetic leather
- Clear bottles
- Floor covering

- Phonograph records
- Water pipe
- Waterproof clothing

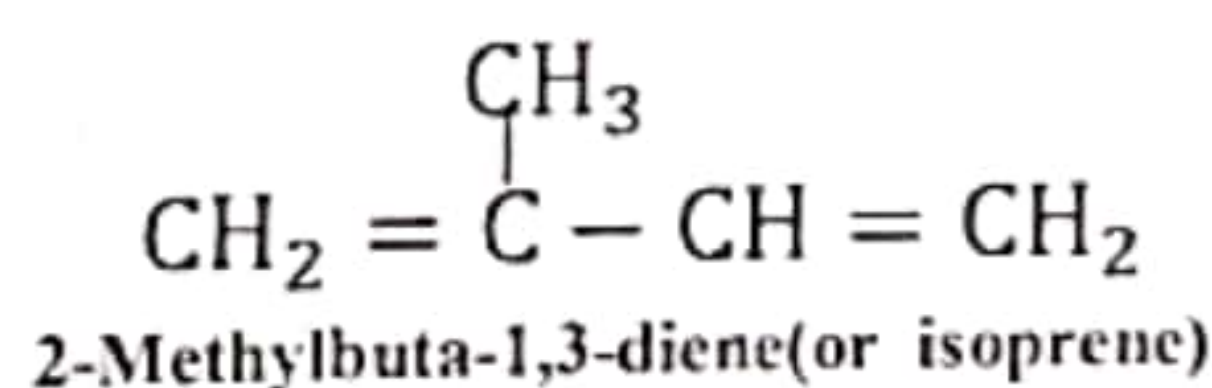
Teflon is used in

- Nonstick surfaces
- Chemically resistant films

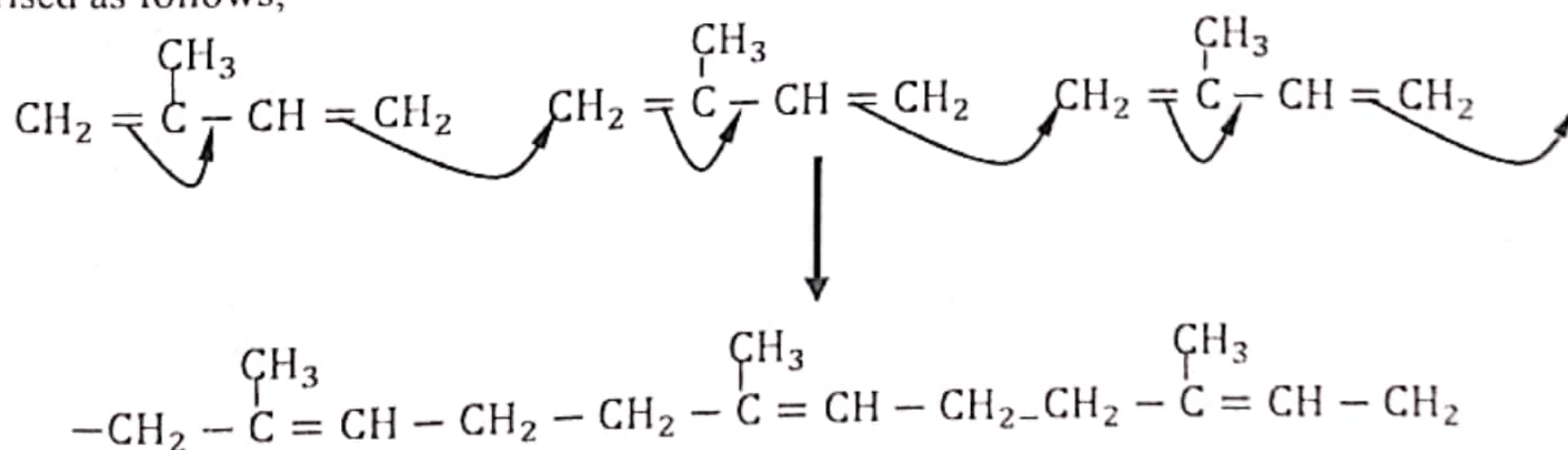
- Artificial arteries and veins

Natural rubber

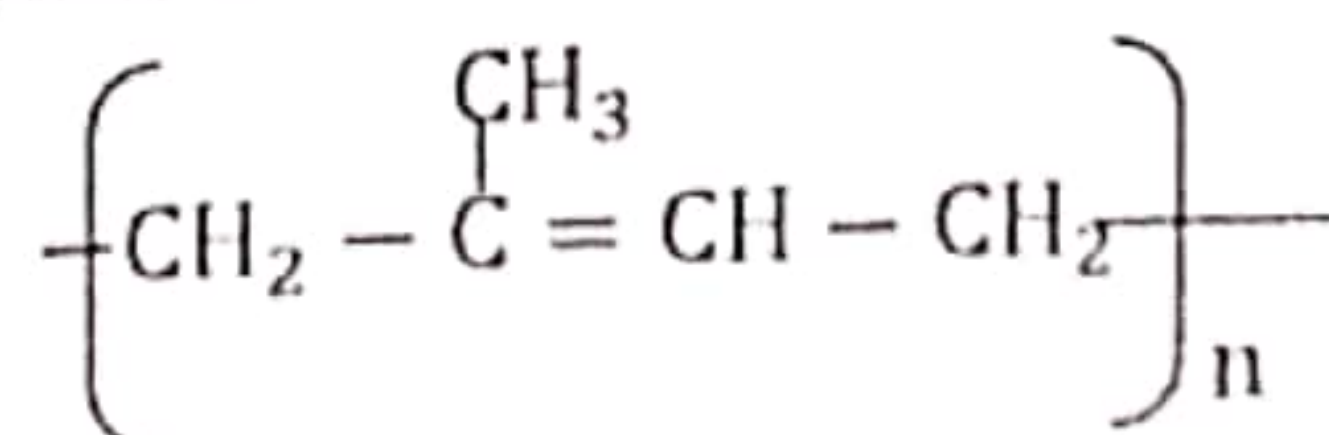
Natural rubber (alternatively known as **India rubber**, **cautchouc** or **raw rubber**) is another important addition polymer whose monomer is 2-methylbuta-1,3-diene (common name is isoprene).



Formation of the natural rubber (poly(2-methylbuta 1,3 diene) or polyisoprene) can be simplified and summarised as follows;



From which repeating unit of the polymer is



And the overall reaction equation is



Vulcanisation of rubber

The long chain molecules of the raw rubber are too soft and sticky to be of much practical use, especially when warmed, why?

This is because the rubber consist of uncrossed chain which can move independently relative to each other.

- Raw rubber (natural rubber) is converted into a tough useful product by the process known as vulcanisation, *what is the vulcanisation of rubber?*

Generally **vulcanisation** (also spelled **vulcanisation**) is the chemical process of converting rubber or related polymer into more durable materials through addition of sulphur or other equivalent curatives or accelerators.

- And specifically, **vulcanisation of rubber** is the chemical process which involve treating rubber with sulphur and heat, thereby imparting strength, greater elasticity and durability.

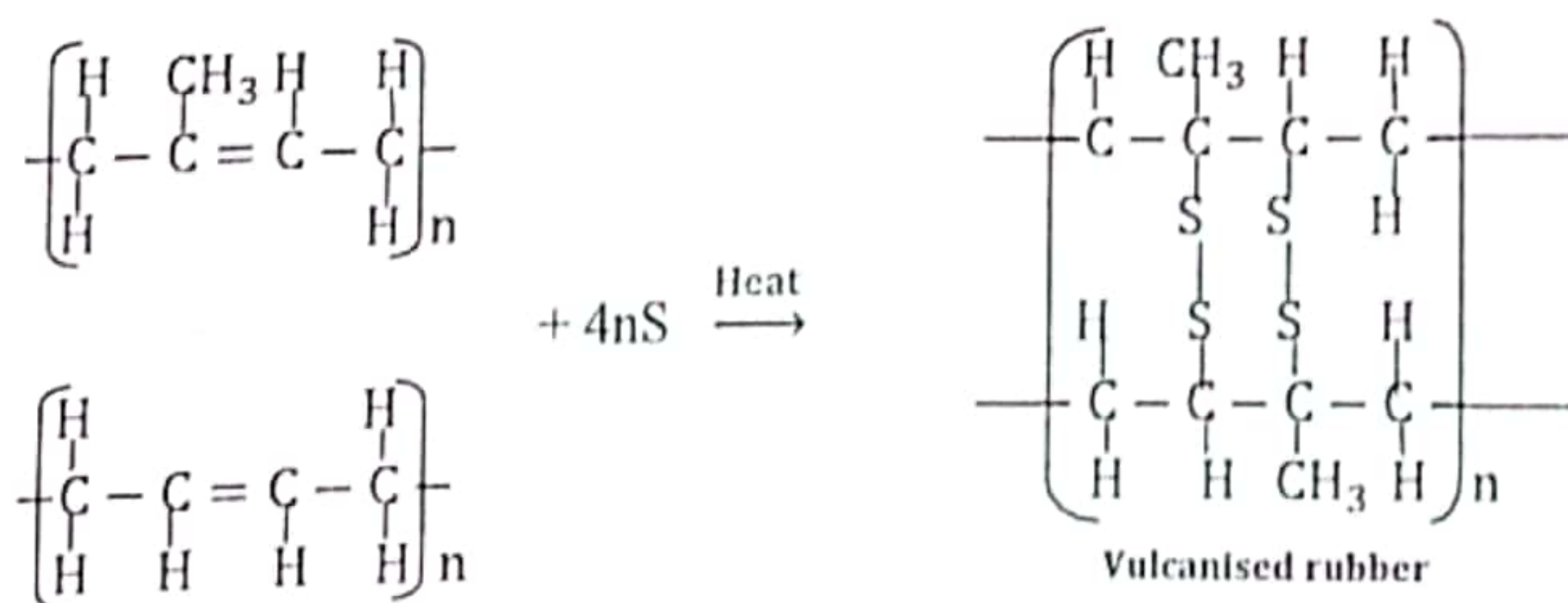
Rubber which has been treated with sulphur in such process is known as **vulcanised rubber (commercial rubber)**.

- Vulcanisation of rubber improves its elasticity, toughness, strength and enables it to be used over a wide range of temperature.

How vulcanisation of rubber is carried out?

Unsaturated nature of natural rubber allows sulphur atoms to be added at double bonds of adjacent chains which appears like a bridges of sulphur between the chains.

- So the vulcanisation is done by mixing sulphur with the raw rubber and then the mixture is heated carefully resulting to formation of bridges of sulphur atoms between adjacent chains at double bond.



Cross linking introduced by vulcanisation, strengthen the rubber because it prevents the polymer chains from moving independently.

Nomenclature of simple addition polymers

In most cases polymers are named by using common names. However IUPAC name had provide a guide for systematic nomenclature of the polymers.

- The complete set of rules of IUPAC nomenclature of polymers is beyond the scope of this book. However it easy to understand rules of naming simple addition polymers as outlined below.

Rule 1:

Name of the simple polymers is derived from its monomer unit with the prefix poly coming before the name of monomers

- For example if the polymer is derived from ethene monomer, the name of the polymer become polyethene.

Rule 2:

If there is at least one **locant** (number representing position of attached or functional group) in the monomers then the monomer name must be enclosed in brackets.

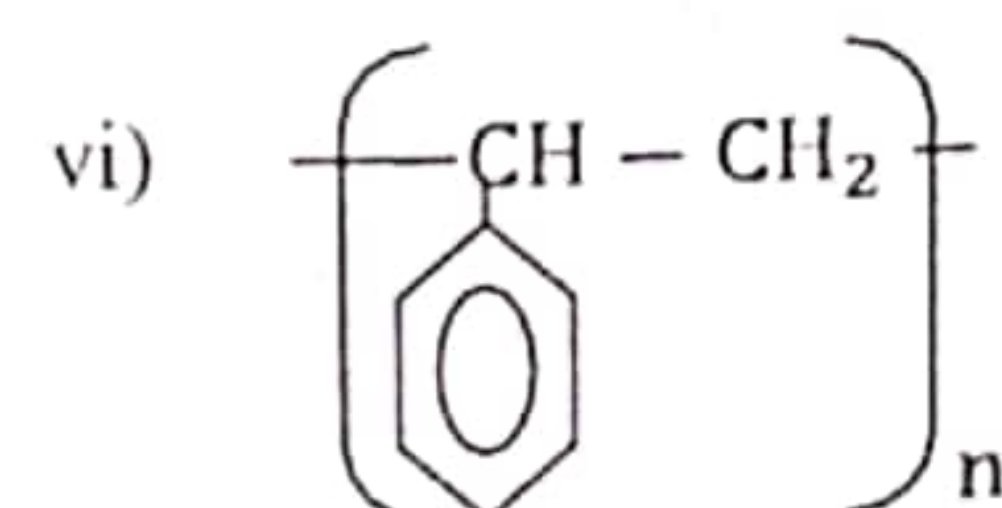
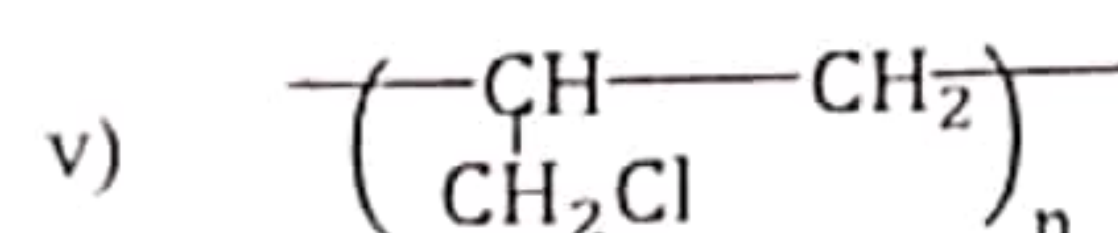
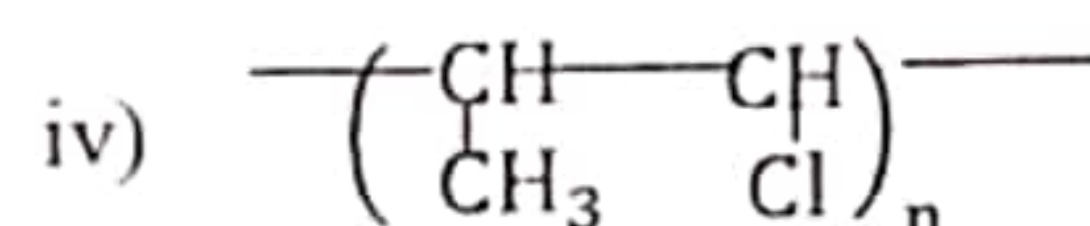
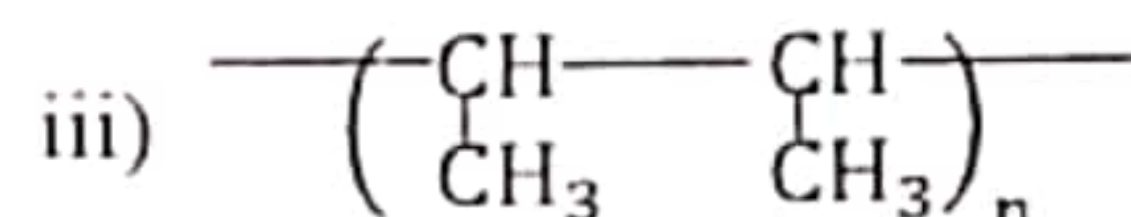
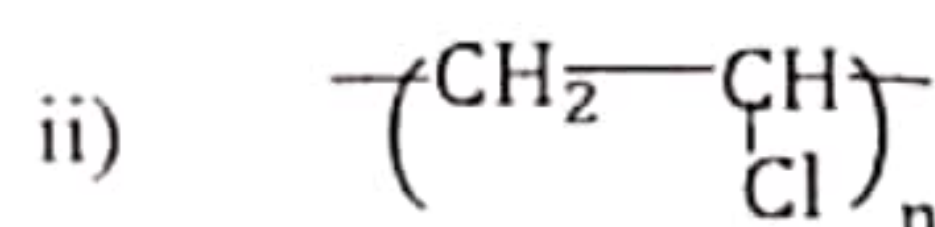
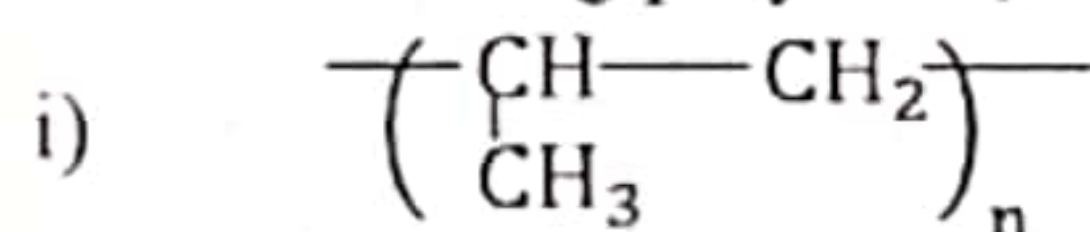
- For example if the monomer of the simple polymers is $\text{CH}_3\text{CH}=\text{CHCH}_3$ (but – 2 – ene), then the polymer is named as poly(but – 2 – ene) and **not** polybut – 2 – ene.

Rule 3:

If there is no any locant in the name of monomer, then it is not necessary to enclose the name in the brackets.

Example

Name the following polymers;-



Solution

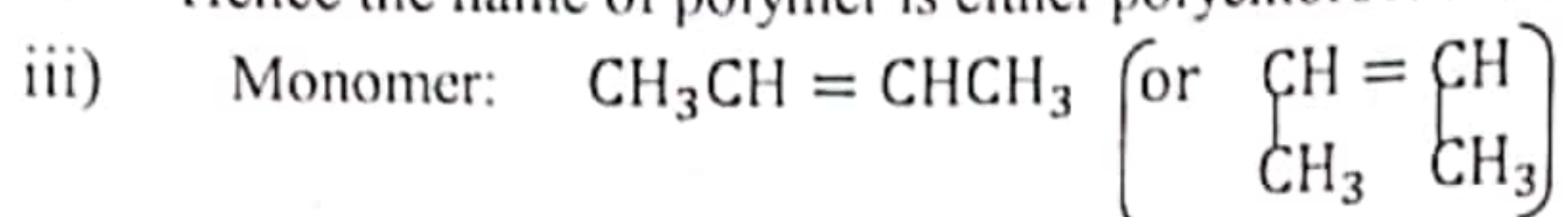
- i) Monomer which will give this polymer is $\text{CH}_3\text{CH}=\text{CH}_2$
(To make this clearer you may rewrite this as $\begin{array}{c} \text{CH} = \text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$)

- Then name of monomer is propene (common name: propylene)
- Hence the name of polymer is either polypropene or polypropylene

- ii) Monomer which will give this polymer is $\text{CH}_2=\text{CH}-\text{Cl}$ (or rewrite $\text{CH}_2=\begin{array}{c} \text{CH} \\ | \\ \text{Cl} \end{array}$)

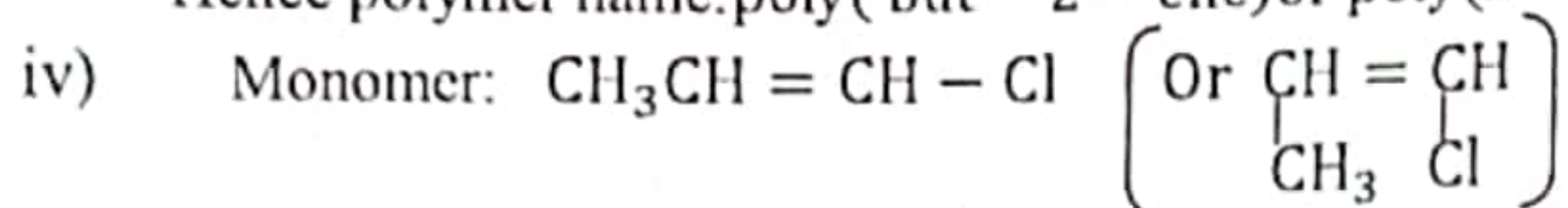
- Name of the monomer is chloroethene (or vinyl chloride as common name)

– Hence the name of polymer is either polychloroethene or polyvinylchloride



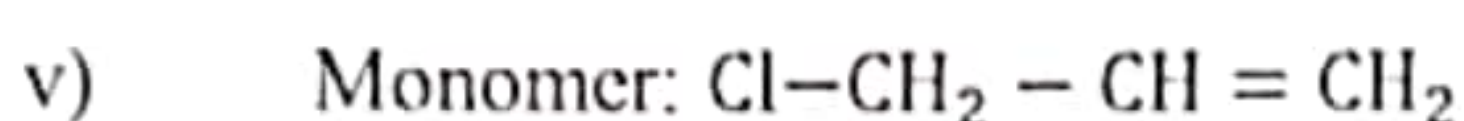
Name of monomer: but – 2 – ene or 2 – butene

Hence polymer name: poly(but – 2 – ene) or poly(2 – butene)



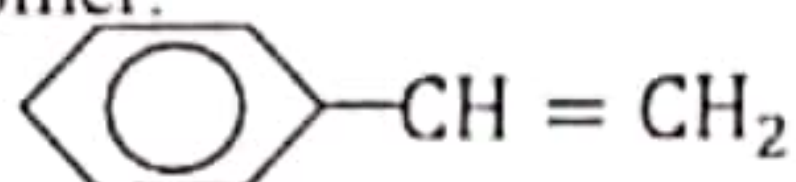
Name of monomer: (1 – chloropropene)

Hence polymer name: poly (1 – chloropropene)



Name of monomer: 3 – chloropropene

Name of polymer: poly (3-chloropropene)



Monomer name: phenylethene or vinylbenzene (or styrene as common name)

Polymer name: polyphenylethene or polyvinylbenzene or polystyrene

Condensation polymerisation

This is the type of polymerisation which involves combination of two or more monomers accompanied with evolution of small molecule; mainly water molecule is evolved.

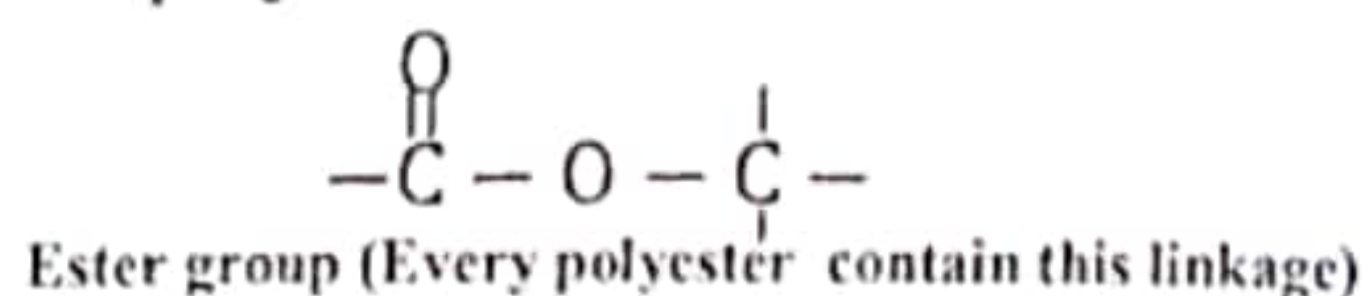
– Small molecules produced in condensation polymerisation are known as **condensate**.

Condensation polymerisation always occurs step-wise where monomers first form dimers then trimers, **oligomer** (a polymer whose molecules consist of relatively few repeating units) and eventually long chain polymer, hence the term **step –growth polymerisation** for condensation polymerisation.

- Condensation polymers may further classified into two main categories;
- Polyesters and
- Polyamides

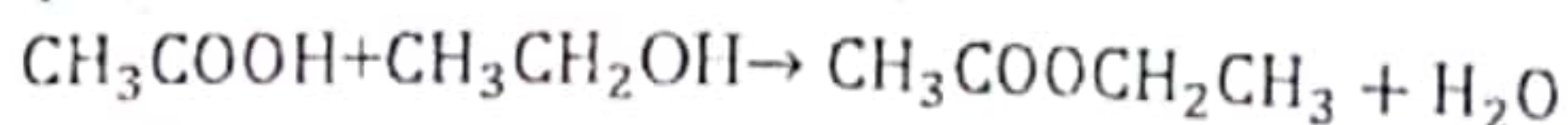
Polyesters

Polyester is a polymer where the monomers are linked together by ester group.

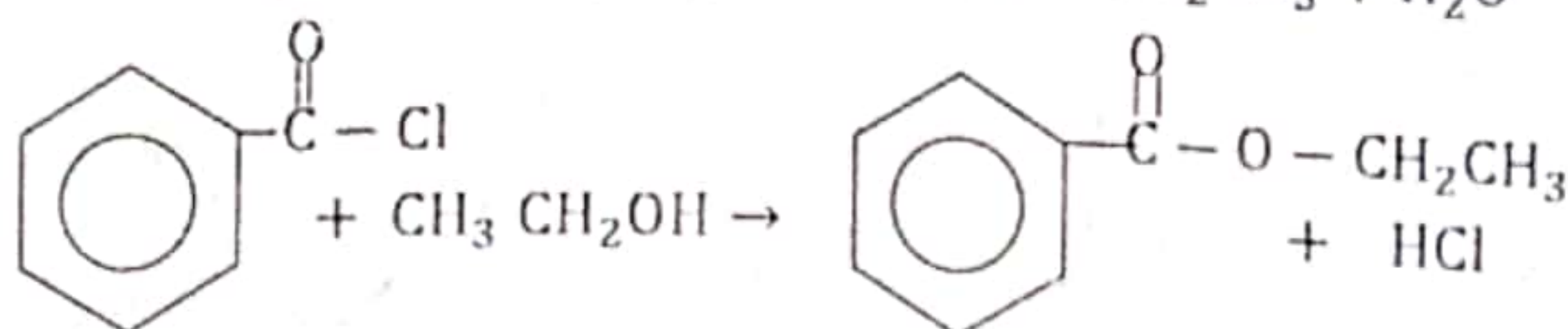


We had studied that if carboxylic acid (or acyl compound) is reacted with an alcohol then an ester is formed and water molecules or (HCl for acyl compound) is given off.

- For example;

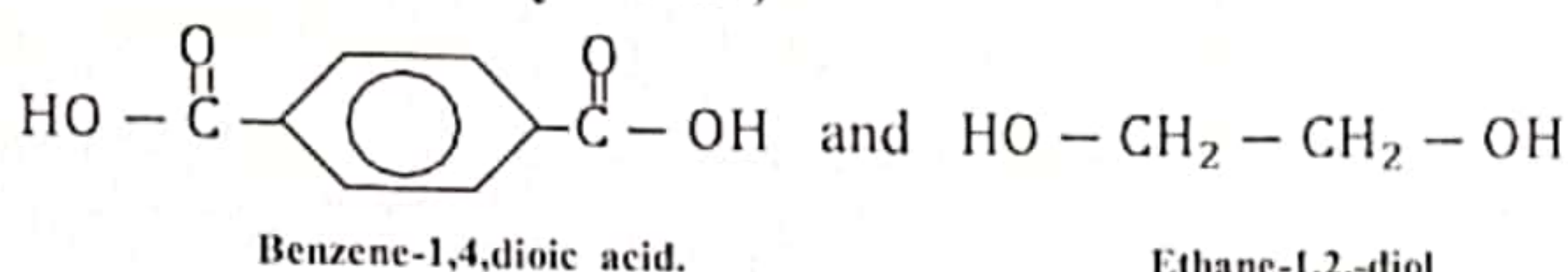


Or

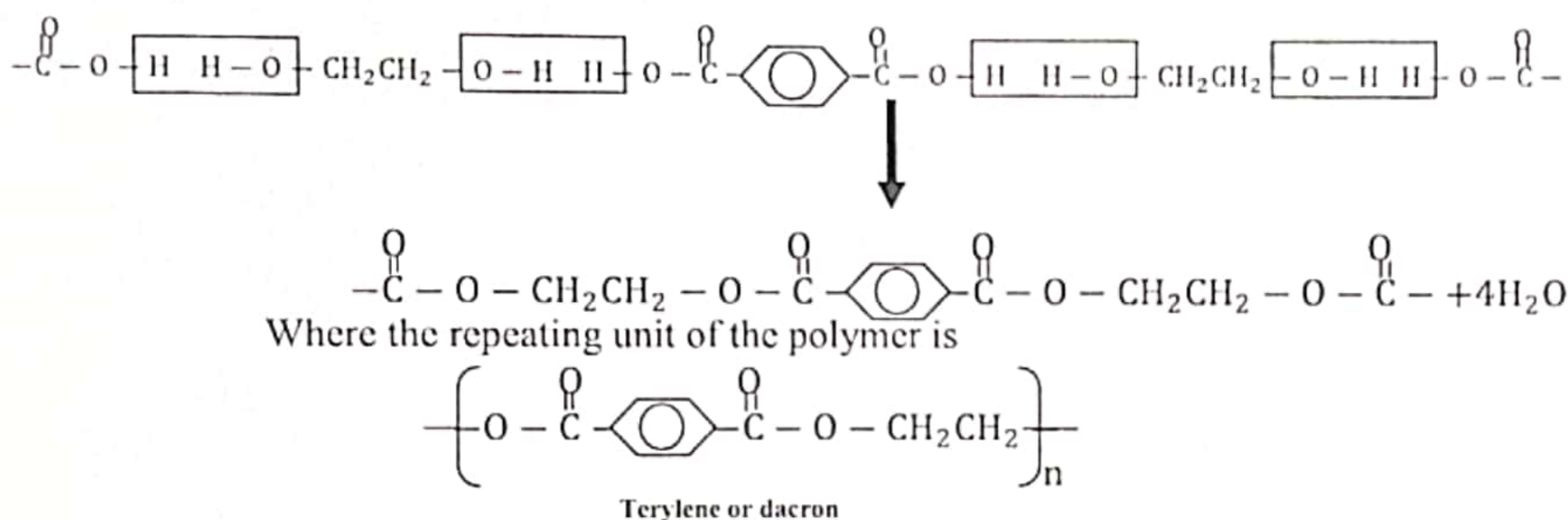


The above two reactions are examples of condensation reaction.

- It follows that if a dicarboxylic acid is reacted with diol then the carboxylic group ($-\text{COOH}$) at each end of dicarboxylic acid will join to a hydroxyl group ($-\text{OH}$), and the $-\text{OH}$ group at each end of the diol should join to $-\text{COOH}$ group and hence become possible for all molecules to link together to form a polymer.
- To have better understanding consider formation of **terylene** (or **Dacron**) as shown below.
- Monomers for formation of **terylene** are:-

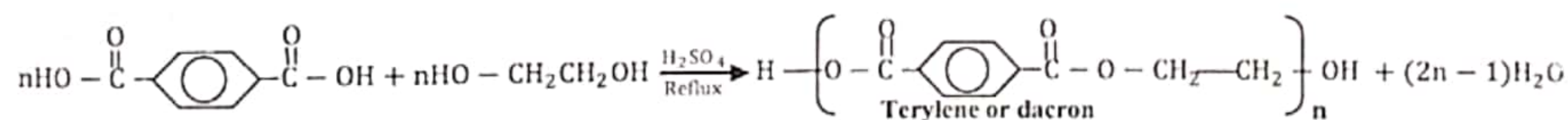


- The two monomers can link together to form a polymer (terylene) and water is given off as follows;

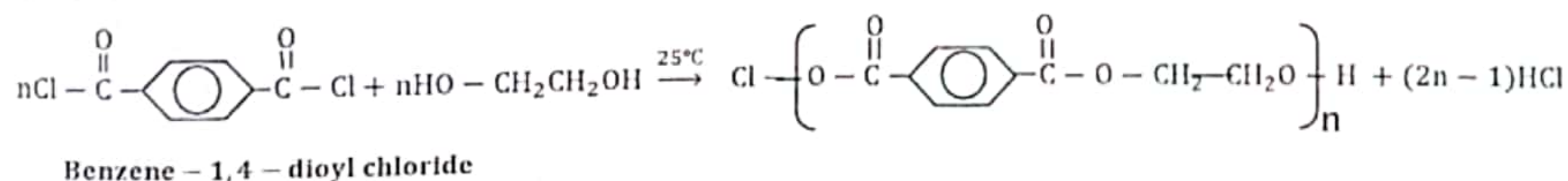


Where n is the degree of polymerisation.

And the overall reaction equation can be represented as follows;



Using the fact that ester can also be formed from the reaction between acyl compound (diacyl chloride) alcohol, the same polymer can also be formed from the combination of benzene - 1,4 - diol and ethane - 1,2 - diol as per equation; (The only difference is that HCl is given off instead of H_2O).



The reader should understand that:

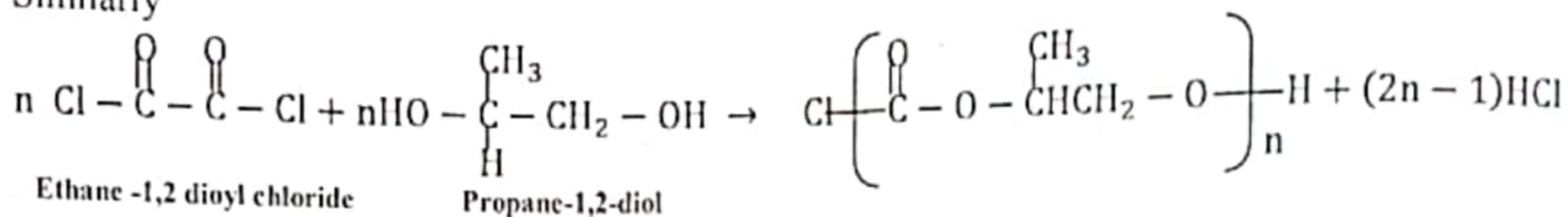
The polymerisation with diacyl chlorides (in this case benzene – 1,4 dioyl chloride) produces a much better yield than the corresponding polymerisation with dicarboxylic acid, *why?*

This is because:

- Acyl chlorides are more reactive than carboxylic acids and therefore the polymer is produced at greater rate.
- Acyl chlorides give off HCl which is gaseous and therefore escapes making reverse reaction difficult.

- Hence in practice, dicarboxylic acids are generally converted to diacyl chlorides by addition of PCl_5 before a polymerisation is carried out.

Similarly



Properties of polyester

- They maintain high tensile strength at high temperature
- They have high impact strength
- They have high resistance to fatigue
- They have good solvent resistant
- They have good moisture resistance
- They contain an ester link $(-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-)$ and therefore they behave as esters
- They can be broken down by hydrolysis and where the $\text{C}-\text{O}$ bond breaks
- They are biodegradable

Uses of polyester

(i) In clothing

- Due to its strength and durability, polyester can be blended with other natural fibers such as wool, silk, or cotton to make clothes which have, more comfortable feel.
- Also it is commonly used to make garments and jackets that are to be used in wet and damp environments because it is hydrophobic (water repellent or resistant as it is insoluble)

(ii) In making fibres

Since polyester can be molded into almost any shape, polyester can be built into the insulating fibres like hollow fibres.

(iii) In packaging

- This is the common use of polyester today where it used to make plastic bottles (PET)
- PET (polyethylene terephthalate) is recyclable and therefore the production of plastic from polyester has been increased much.

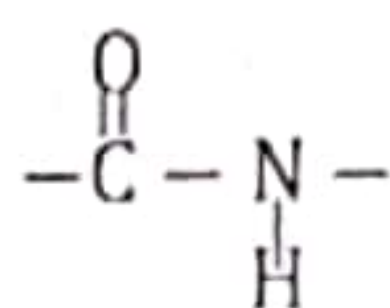
Other uses of polyester

By exploring the properties of polyester, polyester has many other uses. This includes making of:

- | | |
|--------------------------------|--|
| ▪ Carpets | ▪ Ropes |
| ▪ Filters | ▪ Films |
| ▪ Synthetic artery replacement | ▪ Magnetic recording tapes and much more |

Polyamides

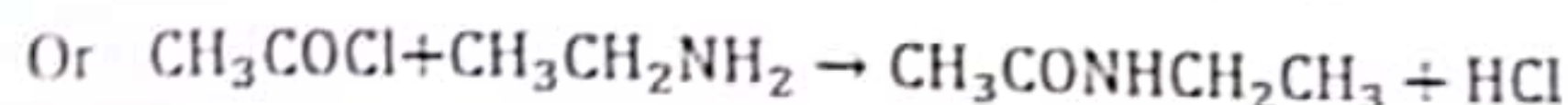
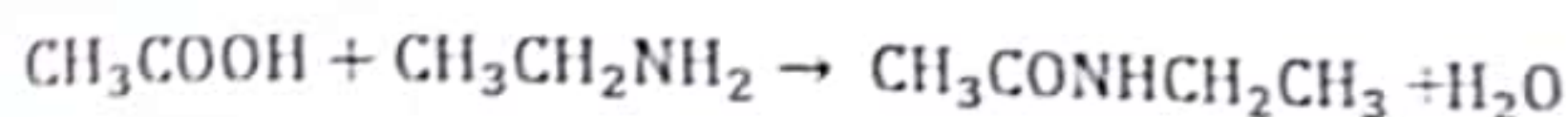
Polyamide is a polymer where the monomers are linked together by the amide.



Amide link in the polyamide

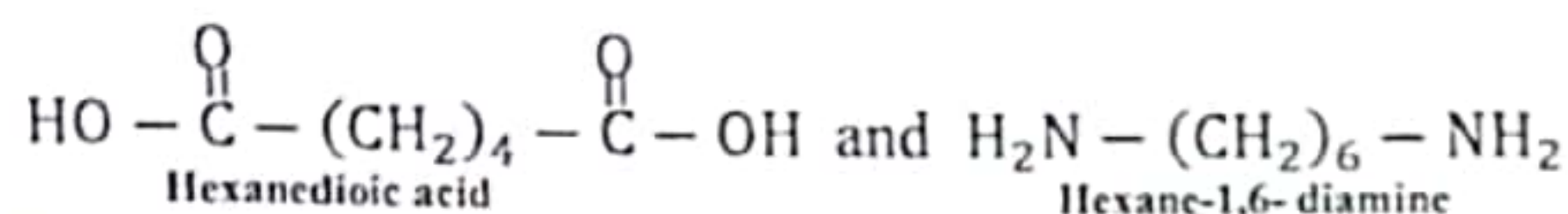
We had studied that if a carboxylic acid or acyl chloride is reacted with primary amine an N-substituted amide is formed.

For example:-

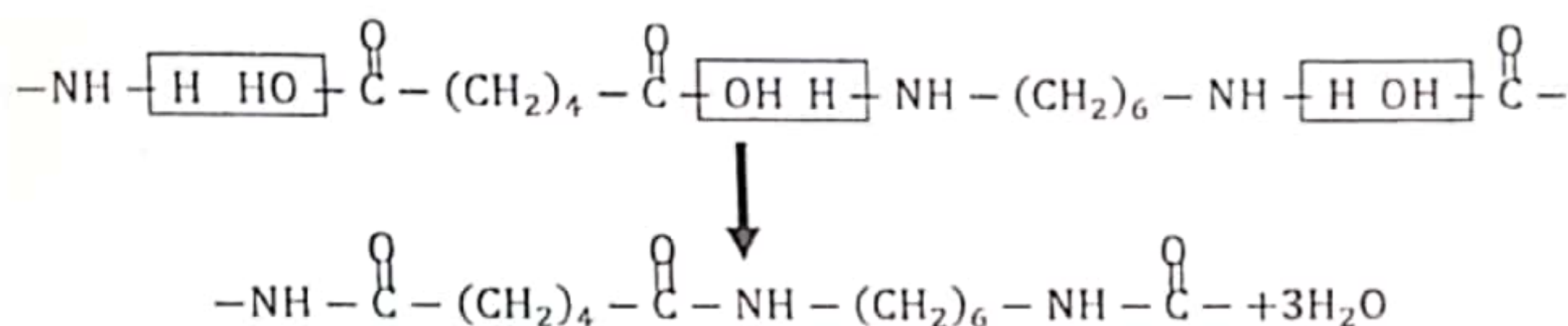


It follows that if a dicarboxylic acid is reacted with diamine, the $-\text{COOH}$ at each end of dicarboxylic acid will join to an $-\text{NH}_2$, and the $-\text{NH}_2$ group at each end of the diamine will join to $-\text{COOH}$ group and hence it become possible for each of molecules to join together to polymer.

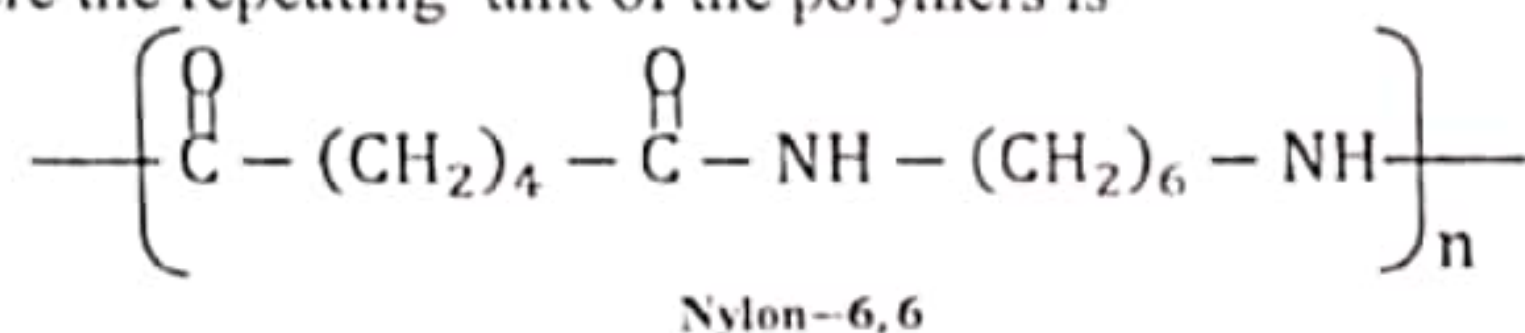
- To have good understanding of this consider formation of nylon - 6,6 shown below:
- Monomers are:



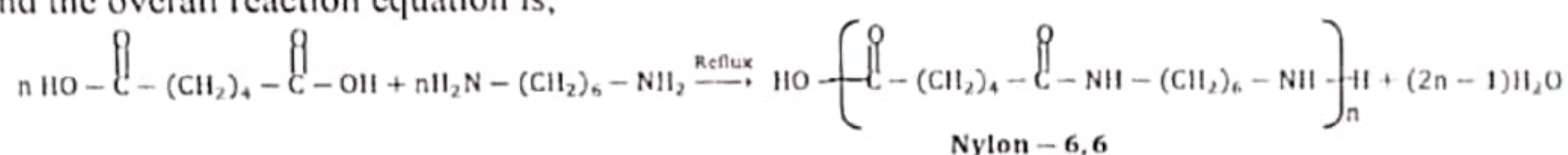
- The two monomers can link to form a polymer(nylon - 6,6) and water is lost as shown below.



Where the repeating unit of the polymers is



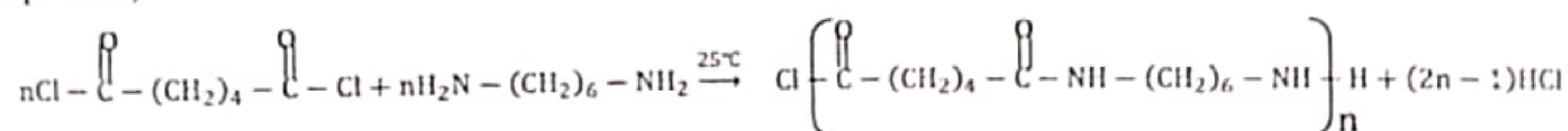
And the overall reaction equation is;



The polymer is called nylon - 6,6 because each of its constituent monomers contains 6 carbon atoms.

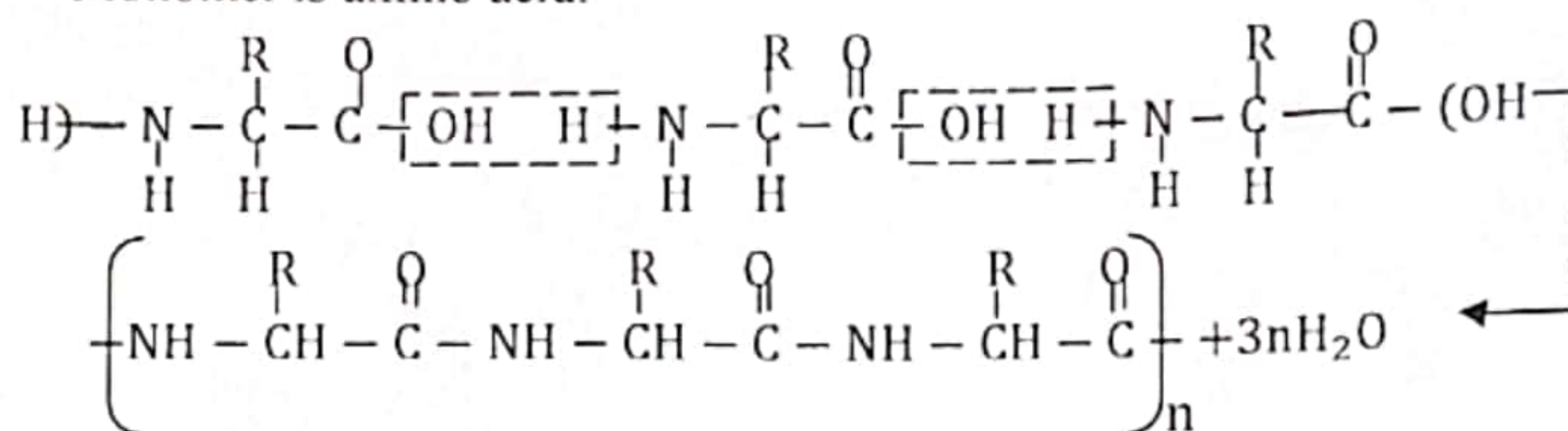
It should be understood that:

The same polymer can be formed by combination of the diacyl chloride and the diamine as per equation;



For the same reasons as in the formation of polyester the polymerisation with diacyl chlorides gives a much better yield than with the corresponding dicarboxylic acid and hence dicarboxylic acids are always converted to the corresponding diacyl chlorides before polymerisation is carried out.

- Another example of polyamide is **protein** whose formation is shown below;
- Monomer is amino acid.

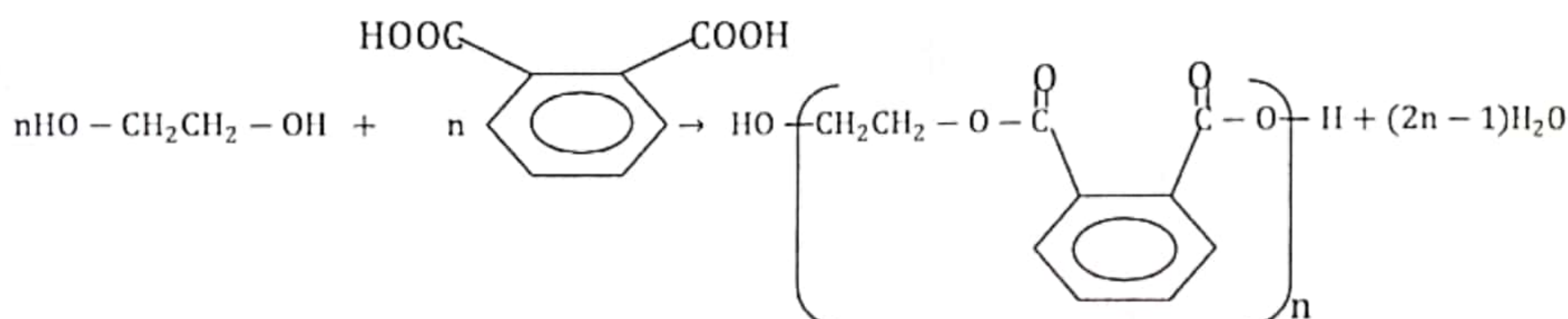


- Another important polyester is glyptal (or alkyl resin) whose monomers are:
 $\text{HO} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{OH}$ and HOOC  COOH

Ethane-1,2-diol

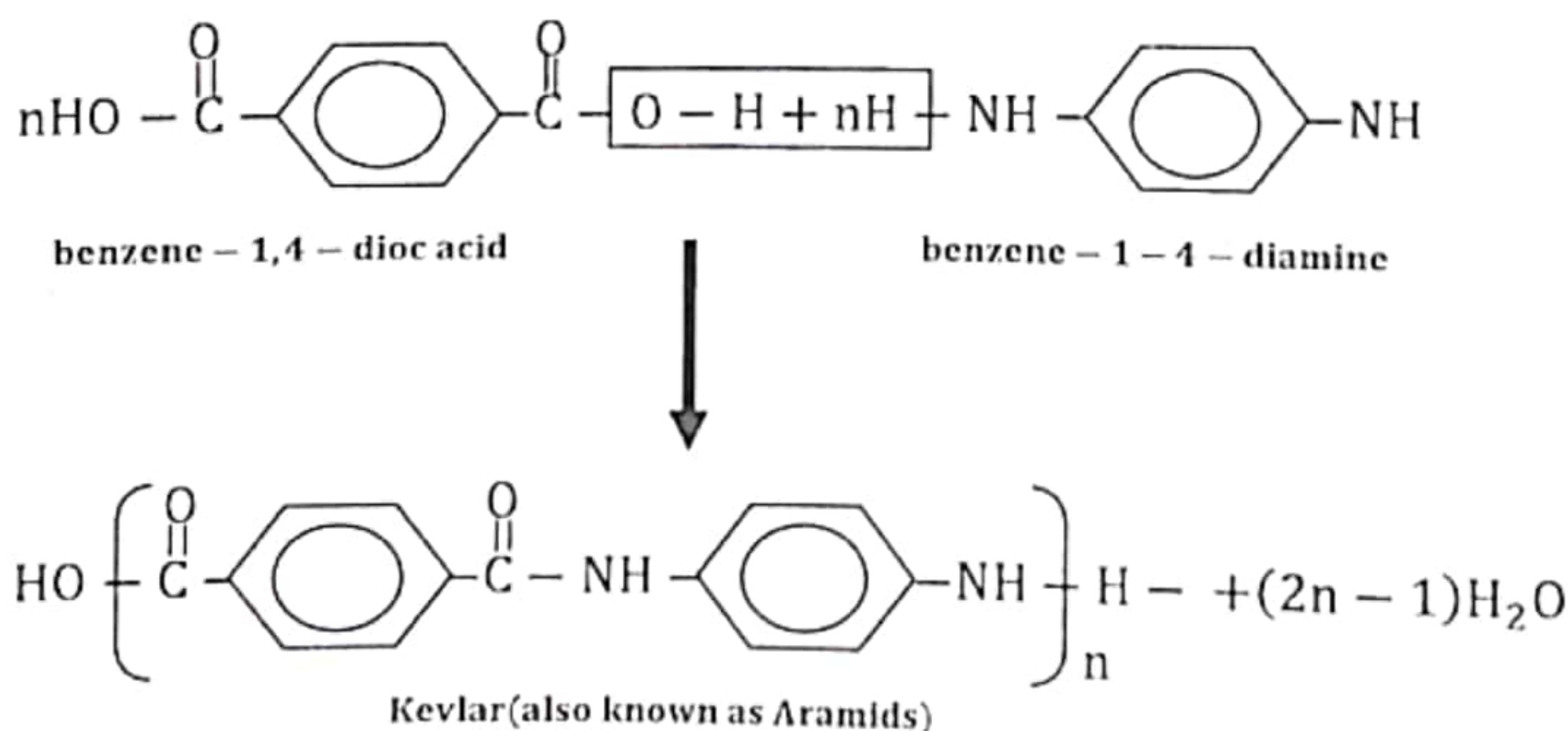
Benzene-1,2-dioic acid

Equation for the reaction:



Glyptal US used in the manufacture of paints and lacquers (A liquid that dries to form a hard protective coating for wood and metal)

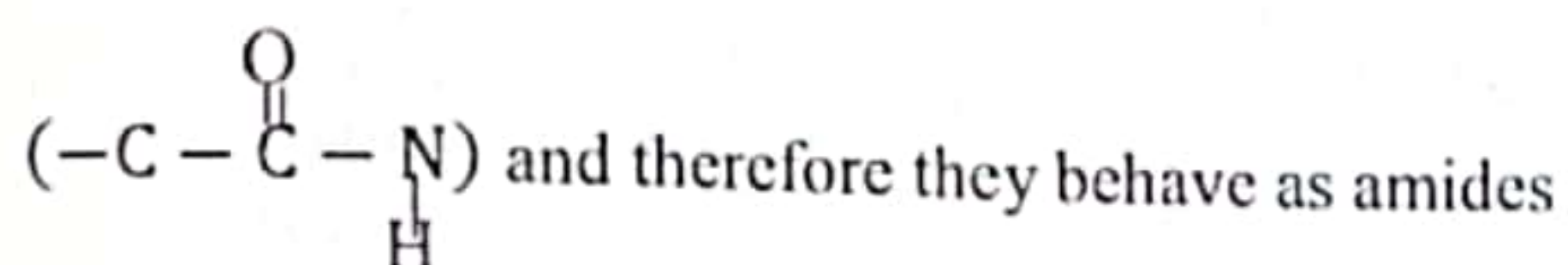
Another example of polyamide is Kevlar whose monomers are benzene - 1,4 - dioc acid and benzene - 1,4 - diamine.



Most of **polyamides** are **nylons** and hence the two terms are often used interchangeably.

Properties of polyamides (nylon)

- Nylon has good tensile strength and elasticity due to presence of hydrogen bonding (Aramids (Kevlar) have much higher tensile strength because apart from hydrogen bonding, Kevlar has aromatic stacking interaction between adjacent polymer chains).
- Nylon have very high melting point (higher than polyester) due to hydrogen bonding.
- Nylons have a low coefficient of friction.
- Nylons are resistant to oil.
- Nylon can absorb moisture (and of course water) thus acting as placticizer.
- They contain an amide (a peptide) link



- vii) They can be broken down by hydrolysis where the C – N bond breaks
- viii) They are biodegradable.
- ix) They have hydrogen bonding between polymer chains.

Uses of polyamides

Most of polyamides are used as fibres in:

- Clothing
- Bullet proof vests
- Carpeting
- Rope

Other uses of polyamides are:

- In gears and bearings
- Protein is natural polyamide which is vital in biochemistry.
- In wheels

The reader should understand that:

Nylon is ideal for making fibres because;

- The amide links in the back bone are themselves strong
- Hydrogen bonds forms between the polymer chains and when the fibre is stretched and then released, this bond re-form to bring the nylon molecules back to their original position, making the nylon elastic (you may notice this in tights under wear).

Kevlar is used as light weight replacement for steel (it is 5 times stronger than steel) because it has very high tensile strength caused by very strong hydrogen bonding between amide group and very flat planar structure means close packing and strong attraction between stacked benzene rings.

Properties of condensation polymers

Compared to properties of addition polymers, properties of condensation polymers have been modified from the following facts:

(i) **Condensation polymers consist largely of straight chains with few branches**

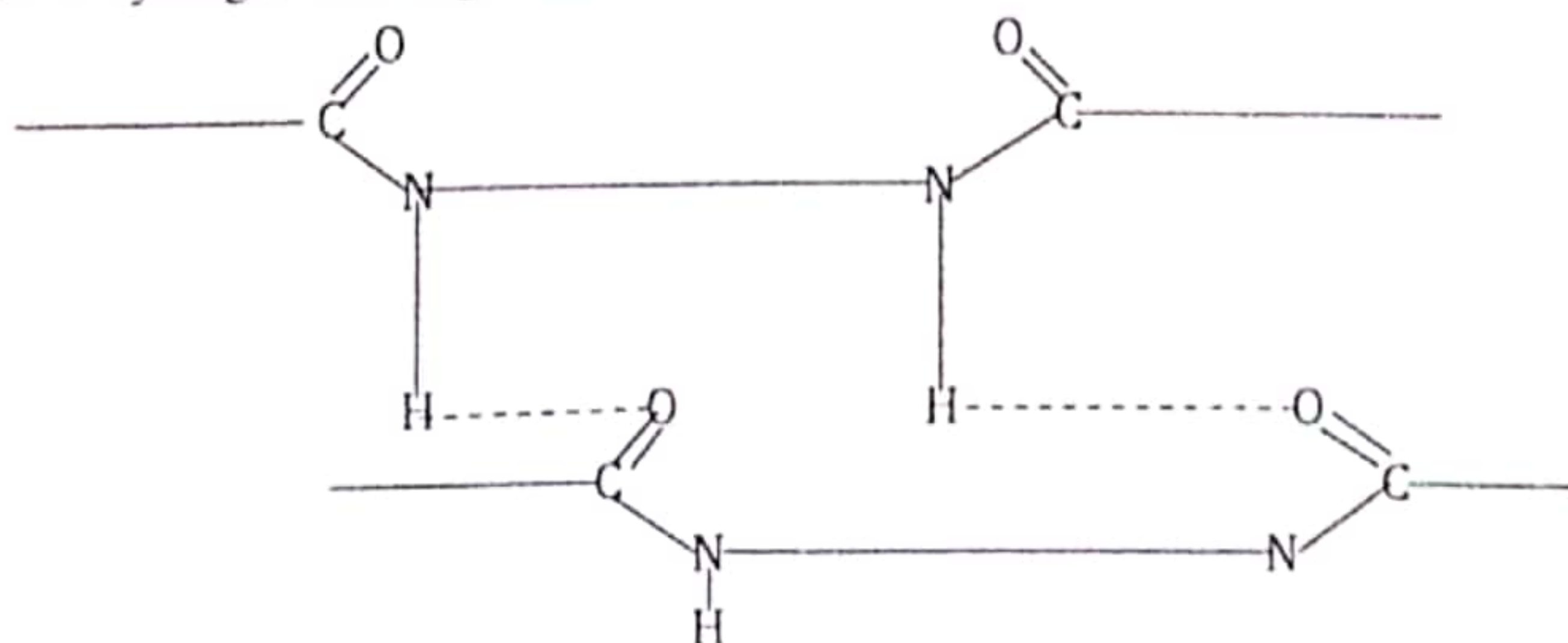
This is because they are formed by reactions with heterolytic mechanisms, which is less random than homolytic mechanism.

- Addition polymers are formed by free radical addition mechanisms which always lead to variety of products and consequently more branching.

Since there are few branches, condensation polymers are linear and therefore pack closely together and hence condensation polymers are more rigid and have high tensile strength than addition polymers.

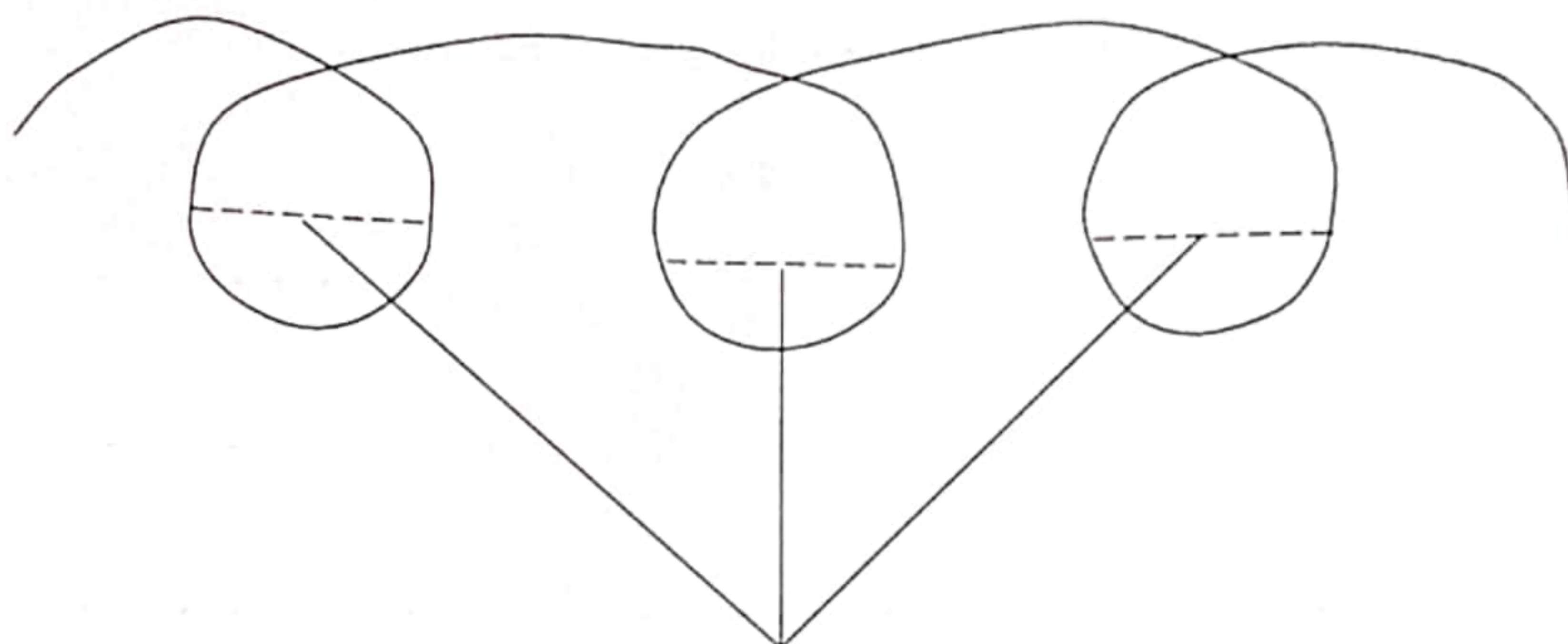
(ii) **Condensation polymers may contain hydrogen bond**

Presence of hydrogen bonding is common in polyamides



Where ----- represents hydrogen bond

In some natural polyamides like proteins, intramolecular hydrogen bonding is possible and therefore the molecules curls up to form a helix (helical structure of spiral)



Intramolecular hydrogen bonding

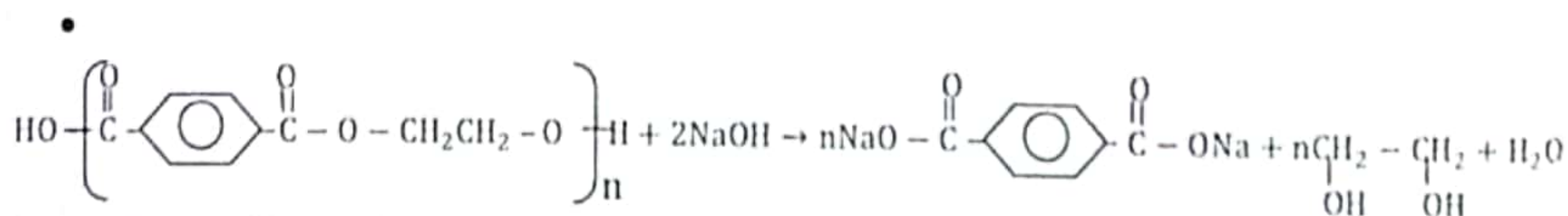
Condensation polymers contain polar bonds!

Condensation polymers are made of chains containing polar bonds

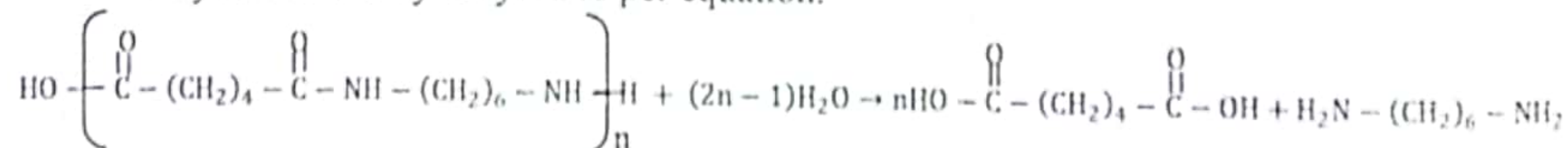
($C^{\sigma+} - N^{\sigma-}$ and $C^{\sigma+} - O^{\sigma-}$ bonds) which link every polymer unit.

- These positive polarised carbon atoms can be easily attacked by nucleophiles and eventually the polymer is broken up and the constituent monomers are reformed. This makes condensation polymer **biodegradable** and hence they contribute a smaller environmental hazard than addition polymers whose chains are made entirely of non polar $C - C$ bond which are hence (with the addition of fact that addition polymers are saturated) **non-biodegradable**.
- The break up of these polymers is carried out in aqueous solution and hence can be classified as hydrolysis reaction as shown below.

Polyesters are hydrolysed in strongly alkaline conditions in which they undergo saponification as per equation.



- Polyamides are hydrolysed as per equation.



Differences between addition and condensation polymers

	Addition polymers		Condensation polymers
01	Formed by addition reaction where by only one molecule is formed	01	Formed by condensation reaction with evolvment of small molecules like H_2O and HCl
02	Molecular mass is a whole number multiple of the monomer.	02	Molecular mass is not whole number multiple of the monomer units
03	Monomers are unsaturated molecules	03	Monomers units must have active functional groups
04	Generally involve one monomer unit	04	Generally involve more than one monomer units
05	They are generally chain growth polymers	05	They are generally step growth polymers
06	They are non-biodegradable	06	They are biodegradable
07	They generally are not reactive	07	They are reactive e.g. they undergo hydrolysis reaction.

Uses of condensation polymers

- Polyamides are useful in making:
 - High strength synthetic fibers
 - Underwear } Because are more elastic
 - Fishing nets }
- Polyesters are useful in:
 - high strength synthetic fibers
 - Wool and cotton substitutes in clothing
 - Bullet- proof vests
 - Flame retardant clothing

DISPOSAL OF NON- BIODEGRADABLE POLYMERS

Methods of disposing polymers depend on whether the polymer is degradable or not.

- **Degradable polymer** is the one that breaks down into smaller fragments when exposed to light, heat or moisture.
- **Biodegradable polymer** is the one that break down completely into carbon dioxide and water under influence of micro living organisms. Most biodegradable polymers are also photodegradable.
- **Photodegradable polymer** is the one that become weak and brittle when exposed to sunlight. It is made by blending the polymer with light sensitive additives which catalyses the breakdown of the polymer in UV light. So when the light hits the polymer the waxy substance forms at first and then eventually micro-organisms (bacteria) convert it to CO_2 and H_2O .

- Condensation polymers are always biodegradable so there is no much problem associated with their disposal as they decompose naturally.
- They can be recycled, broken down into their original components and reused-they are environmental friendly. But they still need to be collected separated and cleaned for healthy environment.

One another hand most of addition polymers are non-biodegradable

- The disposal of non-biodegradable polymers is a big challenging problem. These are three options for disposing these polymers.

First option: by burying in landfill sites

This method is common in many areas.

- However the method is unsustainable practice, as each landfill site will eventually fill up.
- Landfill sites are also unsightly and unhygienic.

Second option: by burning

This is also common in many areas

- However burning polymers releases greenhouse gases such as CO_2
- Also it may release toxic gas like H_2S and SO_2 depending on what exactly polymer is being burned.

Third option: by recycling

This is environmentally preferable to burying or burning but it is not easy.

- Different plastic need to be collected separated and cleaned.
- Then they need to be melted down before being recast into the new item.
- Often this process can cost more than it costs to manufacture the plastic from crude oil.

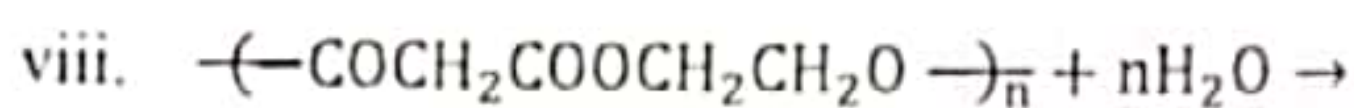
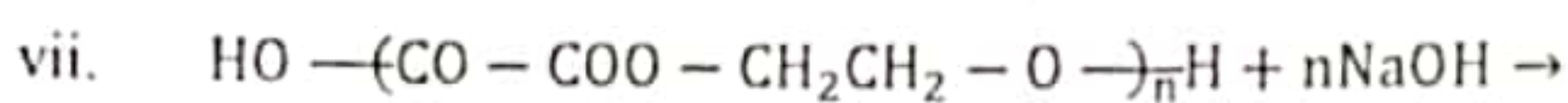
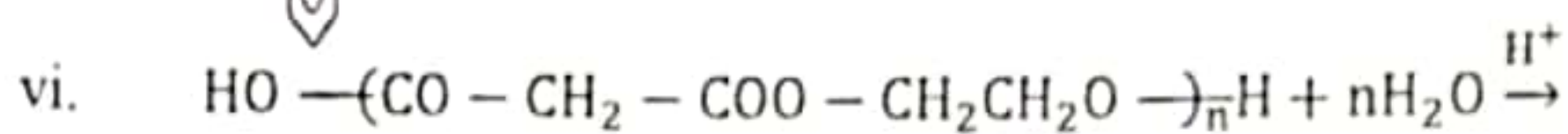
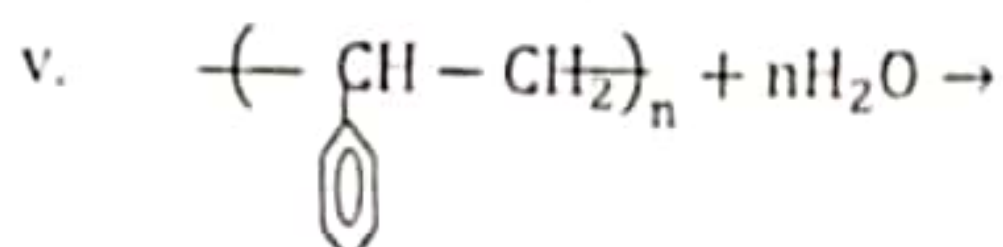
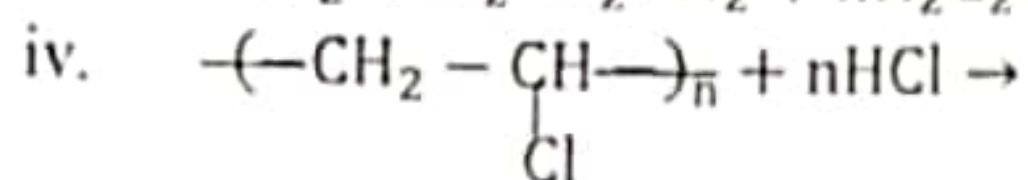
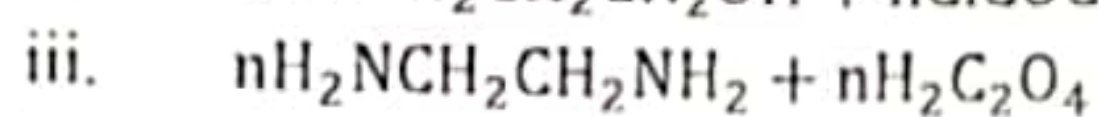
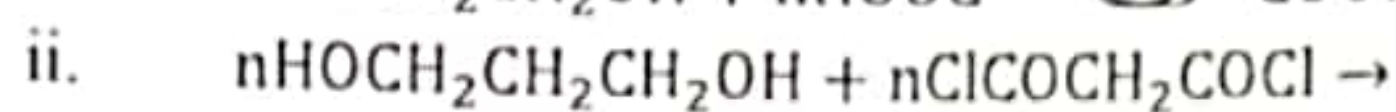
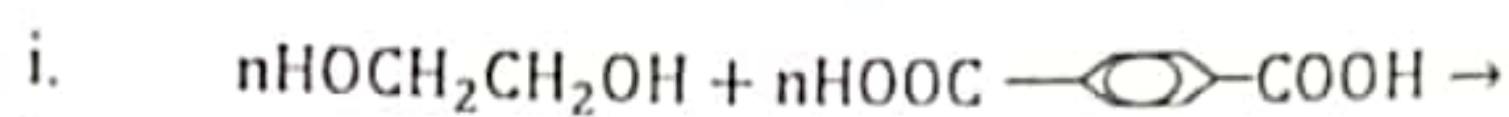
To close the chapter reader should understand that:

Some plastics cannot be melted as they burn or harden instead of melting.

- So it is more difficult to recycle these plastics as they can only be used in the same shape in which they were originally cast.

Problem 5

Complete the following organic reactions;



PART FIVE
MISCELLANEOUS CONCEPTS
ON
ORGANIC CHEMISTRY

Chapter 24

POLYFUNCTIONAL ORGANIC COMPOUNDS

Polyfunctional organic compounds are organic compounds with more than one functional group.

NOMENCLATURE OF ORGANIC COMPOUNDS WITH POLYFUNCTIONAL GROUPS

In naming organic compounds with more than one functional group;

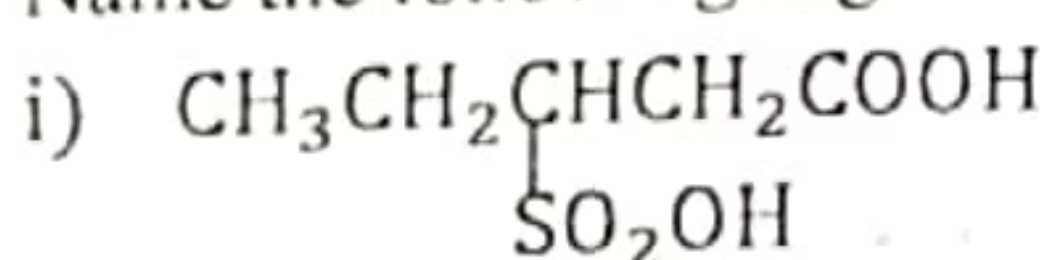
- Parent chain must contain all functional groups.
- The parent name should be that of the most reactive functional group and less reactive functional group should be taken as substituent.
- Carbon with $-\text{CHO}$ or $-\text{COOH}$ and its derivatives should be given first position.

ORDER OF PREFERENCE IN SELECTING MORE REACTIVE FUNCTIONAL GROUPS

CLASS	STRUCTURE	PREFIX	PREFIX ENDING
Quaternary Ammonium salt	$-\text{NH}_4$	—	Ammonium ion
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH}(-\text{COOH}) \end{array}$	carboxy	— oic acid
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR}(-\text{COOR}) \end{array}$	Alkoxy carbonyl	Alkyl alkanoate
Acid halide (Acylhalide)	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{X}(-\text{COX}) \end{array}$	Haloformyl	—oyl halide
Amide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2(-\text{CONH}_2) \end{array}$	Carbamoyl(or amido)	Amide
Nitrile	$-\text{C} \equiv \text{N} (\text{CN})$	Cyano	Nitrile
Sulphuric acid	$-\text{SO}_3\text{H}$	Sulpho	Sulphuric acid
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	Formyl or oxo	—al
Ketone	$\text{C} = \text{O}$	Keto or oxo	—one
Alcohol	OH	Hydroxy	—ol
Amine	$-\text{NH}_2$	Amino	Amine
Ether	$-\text{O}-$	Alkoxy	—
Alkene	$\text{C} = \text{C}$	—	—ene
Alkyne	$-\text{C} \equiv \text{C}-$	—	—yne

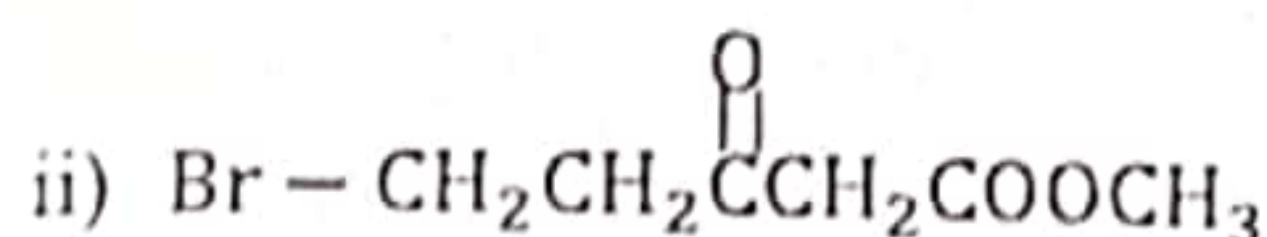
Example 1

Name the following organic compounds



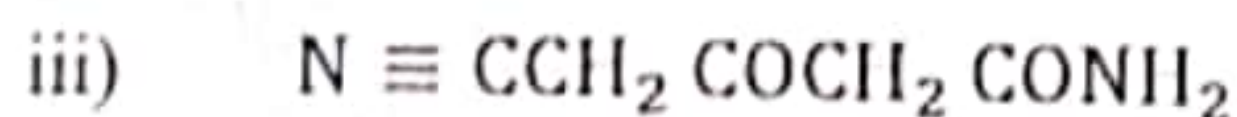
Name: 3-sulphopentanoic acid.

Comments: This compound contains two functional groups whose order of priority is $-\text{COOH} > -\text{SO}_2\text{OH}$. Therefore $-\text{COOH}$ is the principal functional group and $-\text{SO}_2\text{OH}$ is regarded as substituent.



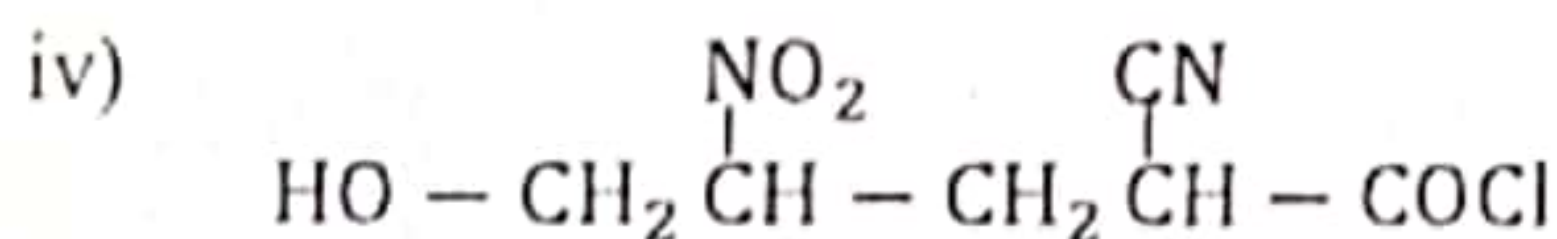
Name: Methyl(5 - bromo - 3 - ketopentanoate) or Methyl(5 - Bromo - 3 - oxopentanoate)

Comments: This compound contains three functional groups whose order of priority is $-\text{COOH} > \text{C} = \text{O} > -\text{Br}$. Therefore $-\text{COOCH}_3$ (Ester) is principal functional group and $\text{C} = \text{O}$ and $-\text{Br}$ are regarded as the substituents.



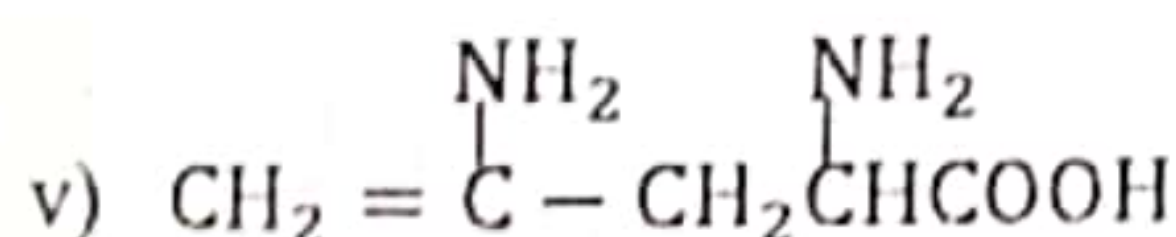
Name: 4 - cyano - 3 - ketobutanamide

Comments: This compound contains three functional groups whose order of priority is $-\text{CONH}_2 > -\text{CN} > -\text{NO}_2$. Therefore $-\text{COOH}$ is principal functional group and $-\text{CN}$, $-\text{OH}$ and $-\text{NO}_2$ are regarded as the substituents.



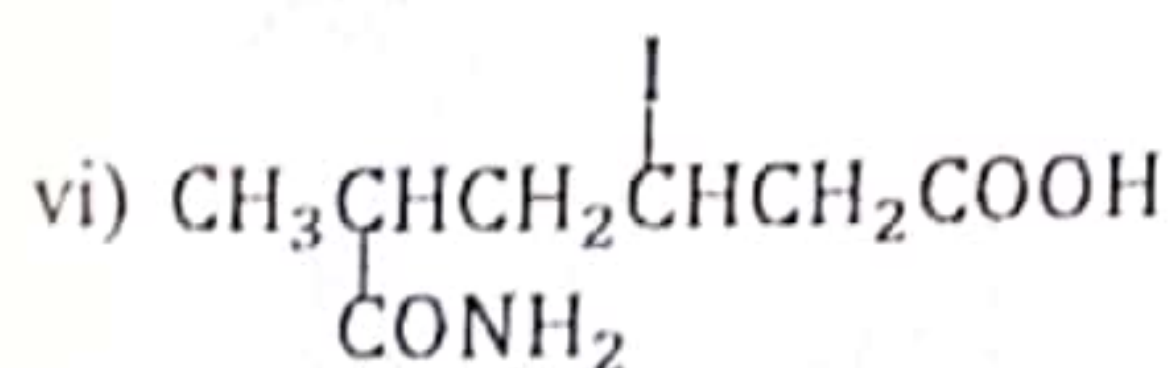
Name: 2 - cyano - 5 - hydroxy - 4 - nitropentanoylchloride

Comments: This compound contains four functional groups whose order of priority is $-\text{COCl} > -\text{CN} > \text{OH} > \text{NO}_2$. Therefore $-\text{COOH}$ is principal functional group and $-\text{CN}$, $-\text{OH}$ and $-\text{NO}_2$ are regarded as the substituents.



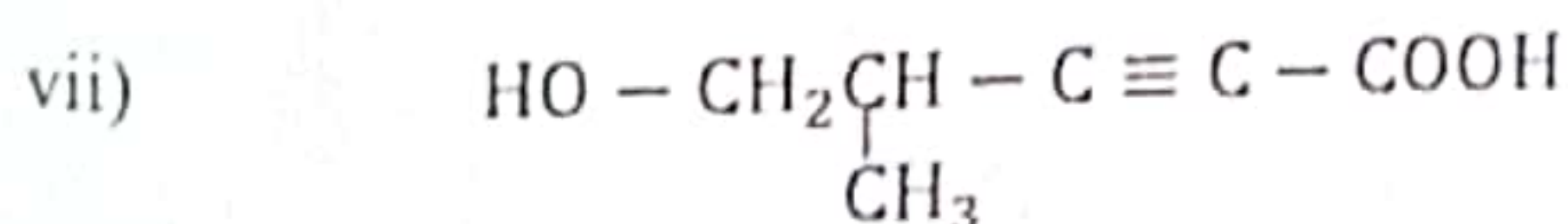
Name: 2,4 - diamino - 4 - pentenoic acid or
2,4 - diaminopent - 4 - enoic acid

Comments: This compound contains three functional groups whose order of priority is $-\text{COOH} > \text{NH}_2 > -\text{C} = \text{C}-$. Therefore $-\text{COOH}$ is principal functional group and $-\text{C} = \text{C}-$ and NH_2 are regarded as the substituents.



Name: 5 - carbamoyl - 3 - iodohexanoic acid

Comments: This compound contains three functional groups whose order of priority is $-\text{COOH} > -\text{CONH}_2 > -\text{I}$. Therefore $-\text{COOH}$ is principal functional group and $-\text{CONH}_2-$ and $-\text{I}$ are regarded as the substituents.



Name: 5 - hydroxy - 4 - methyl - 2 - pentynoic acid or 5 - hydroxy - 4 - methylpent - 2 - ynoic acid.

Comments: This compound contains three functional groups whose order of priority is $-\text{COOH} > -\text{OH} > -\text{C} \equiv \text{C}-$. Therefore $-\text{COOH}$ is principal functional group and $-\text{OH}-$ and $-\text{C} \equiv \text{C}-$ are regarded as the substituents.

Common mistakes made by students in giving iupac name of organic compounds

- Incorrect recognition of parent chain i.e they only check for horizontal chain.
- Numbering carbon wrongly i.e incorrect selection of end of carbon chain for starting numbering carbons.
- Forgetting that carbon with carbonyl group in aldehyde and in carboxylic acids and its derivatives must be given first position.
- Forget naming substituents according to alphabetical order regardless to their positions on their reactivities.
- They forget to use pre-fix di, tri, tetra etc. when there are more than one substituents of the same type.
- They forget to write the name of organic compounds as a single word.
- Incorrect preference of selecting most reactive functional group (for naming organic compounds with more than one functional group).

CHEMICAL REACTIONS OF POLYFUNCTIONAL ORGANIC COMPOUNDS

Chemical reactions of polyfunctional groups organic compounds is the sum of chemical reactions shown by constituent functional groups present in the compound.

- Below are two rules which help to understand formation of products in the reaction of polyfunctional groups of organic compounds.

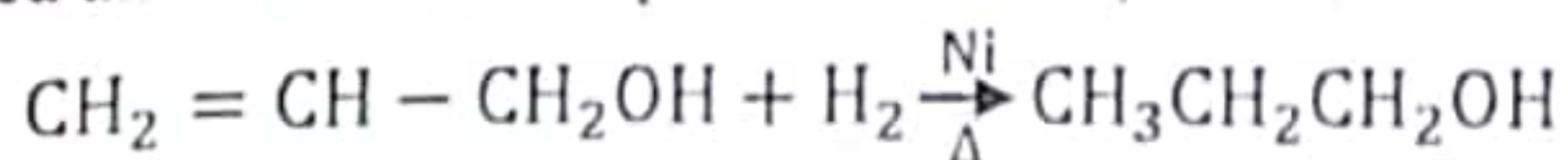
Rule 1:

Only active functional group towards a given reagent will undergo a change in the formation of organic product.

- This rule applies only when only one functional group in the polyfunctional groups organic compound can react with the given reagent and other functional groups has no reaction at all with that reagent.
- To have better understanding of this, consider the reaction of ally alcohol (prop - 2 - en - 1 - ol), $\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$ with the following reagents:
 - H_2 under presence of nickel catalyst and heat
 - PCl_5 under reflux
 - Cl_2 in CCl_4
 - Sodium metal

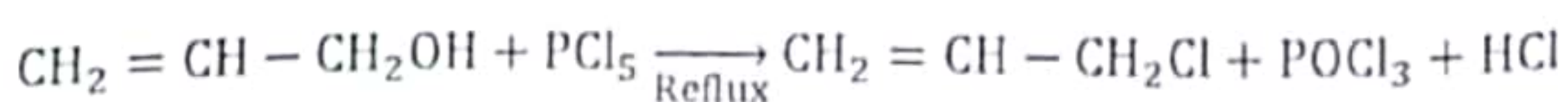
i) With H_2 under presence of nickel catalyst and heat

- Here it clearly understood that the given reagents and condition favours occurrence of hydrogenation reaction.
- And it can be easily remembered that hydrogenation may take place at $\text{C} = \text{C}$ (alkene group) and not OH (alcohol group) and therefore only $\text{C} = \text{C}$ portion of the compound will change leaving the OH portion unchanged and the reaction equation becomes;



ii) With PCl_5 under reflux

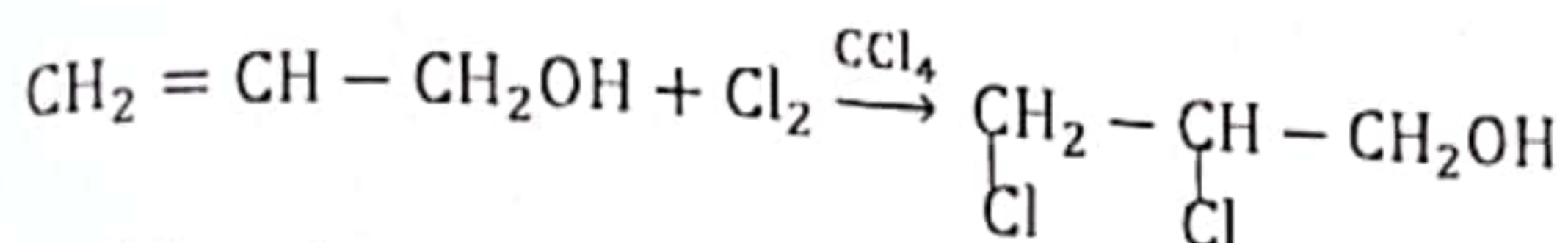
- This is clearly understood reaction for alcohol and not alkenes reaction and therefore the reaction equation becomes;



(Here the OH group has changed while the $\text{C} = \text{C}$ has not changed)

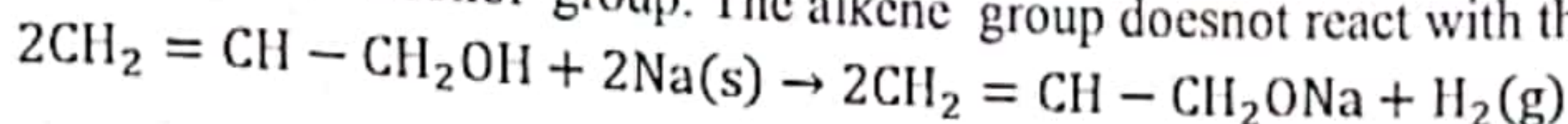
iii) With Cl_2 in CCl_4

- This is clear reaction for alkenes. Alcohol has no reaction to given reagent under given conditions.



iv) With sodium metal

- This is the reaction for alcohol group. The alkene group does not react with the metal



Rule 2:

If a given reagent has action on more than one functional group present in the compound under given conditions, then the more reactive functional group towards that reagent is only one which will undergo a change unless the reagent present in excess where all the reactive groups will undergo changes.

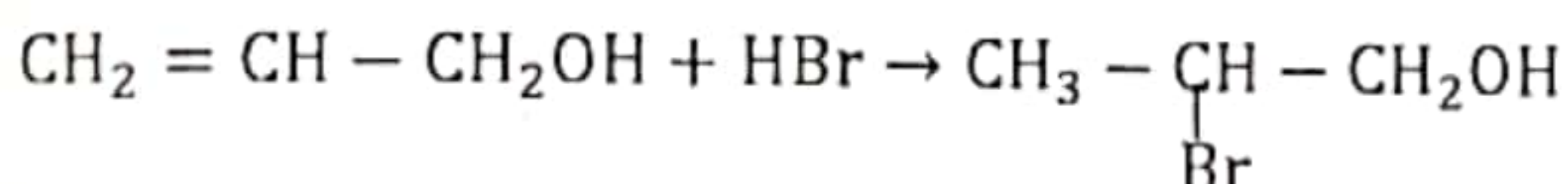
- To have better understanding of this let us return to our example of $\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$. And now assume the compound is allowed to react with :

- Small amount of HBr
- Excess HBr

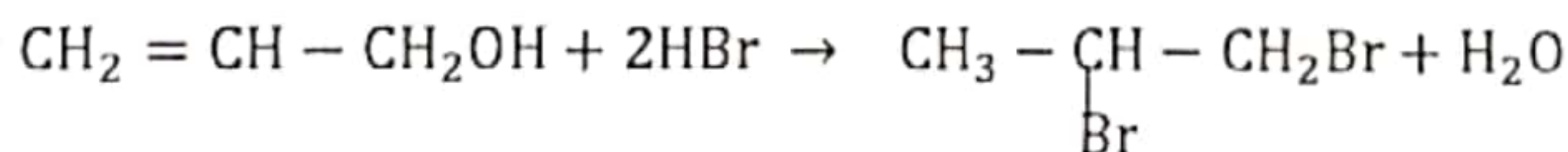
(Here HBr can react with both alkene group and alcohol group)

i) With small amount of HBr

The reaction between alkene and HBr occurs via addition reaction mechanism which is more favoured than substitution reaction mechanism occurring in alcohol (Alcohol group reacts with HBr via nucleophilic substitution reaction mechanism). So if HBr present in small amount only alkene group will undergo a change leaving the alcohol group unchanged.

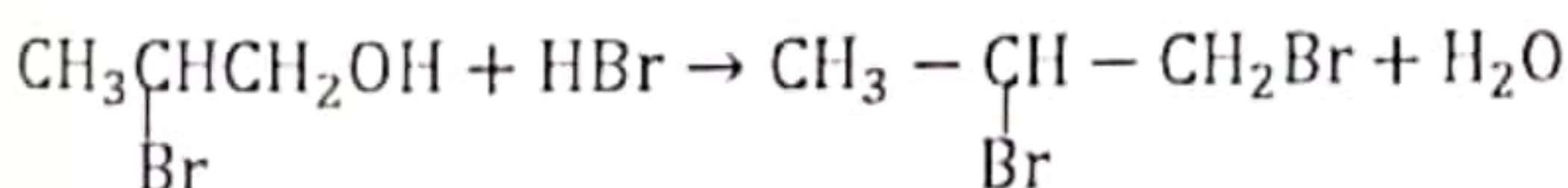
ii) With excess amount of HBr

- Here both alkene and alcohol groups will undergo changes and the overall reaction equation become:



Note:

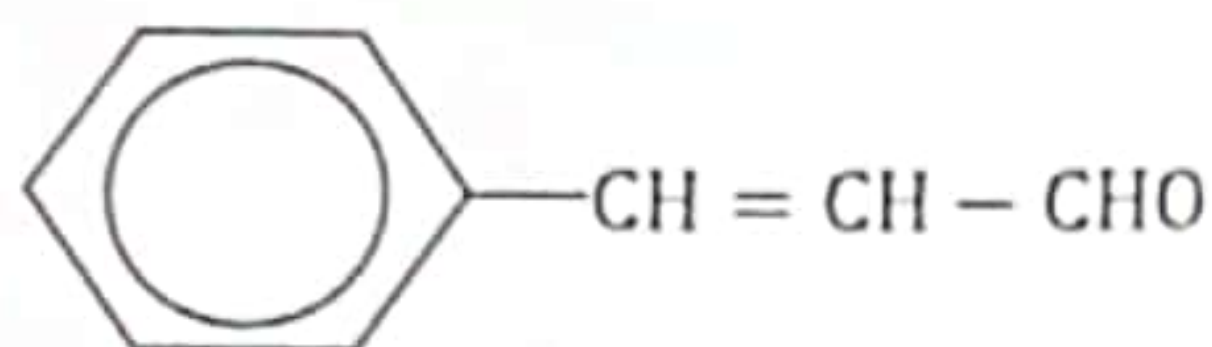
The final product has been obtained after allowing molecule HBr to react with the product obtained in the first case (after adding first molecule HBr)



(obtained after allowing
one molecule of
 HBr to react)

Example 2

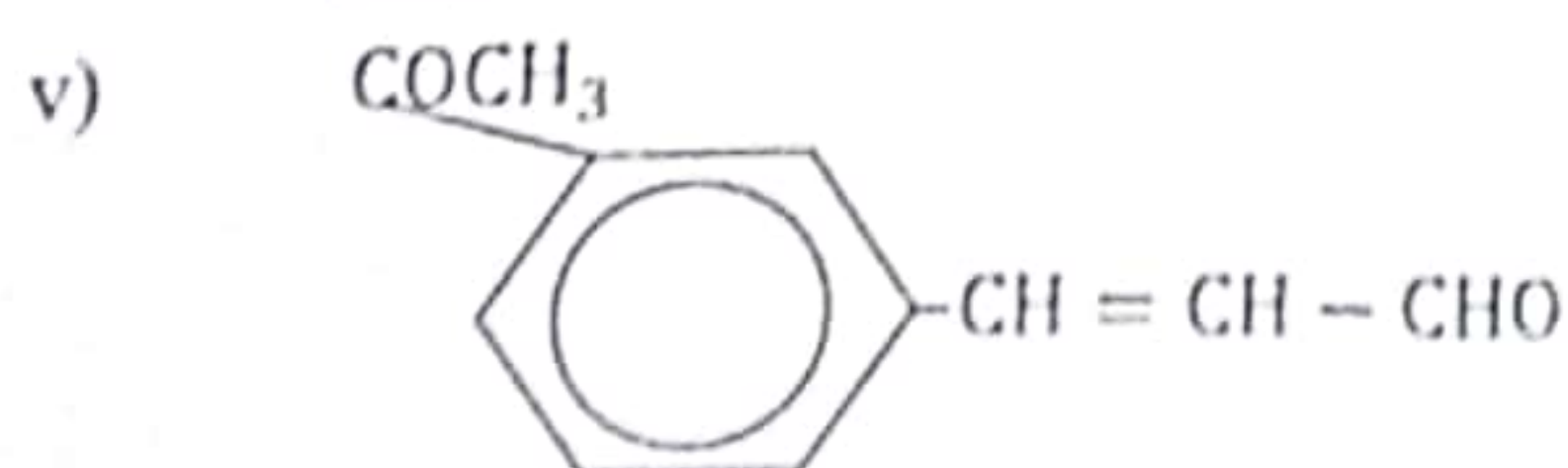
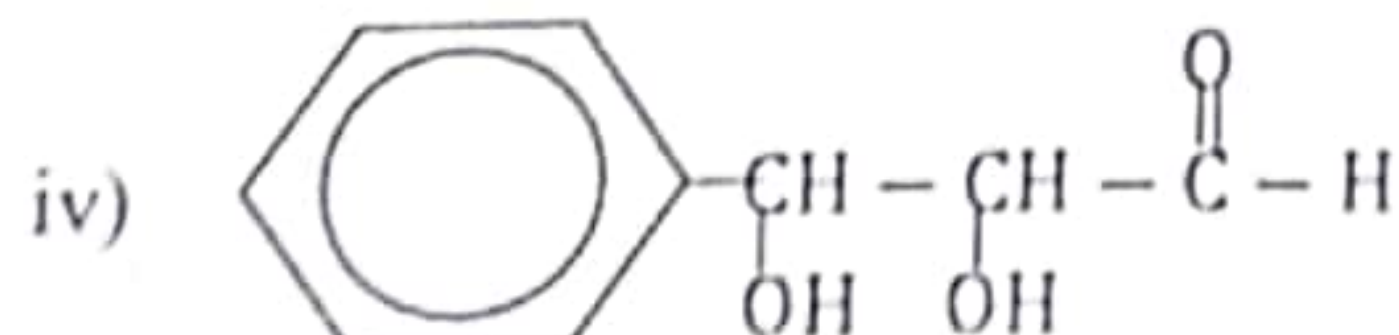
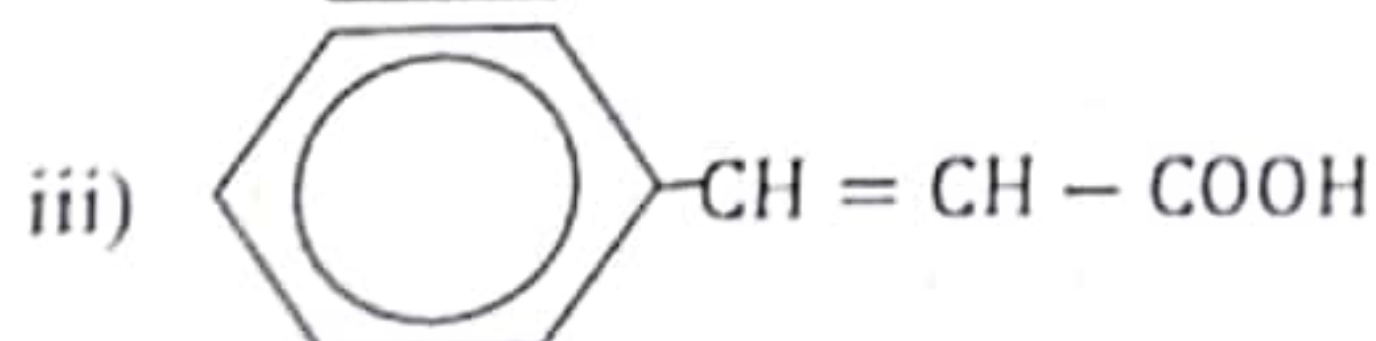
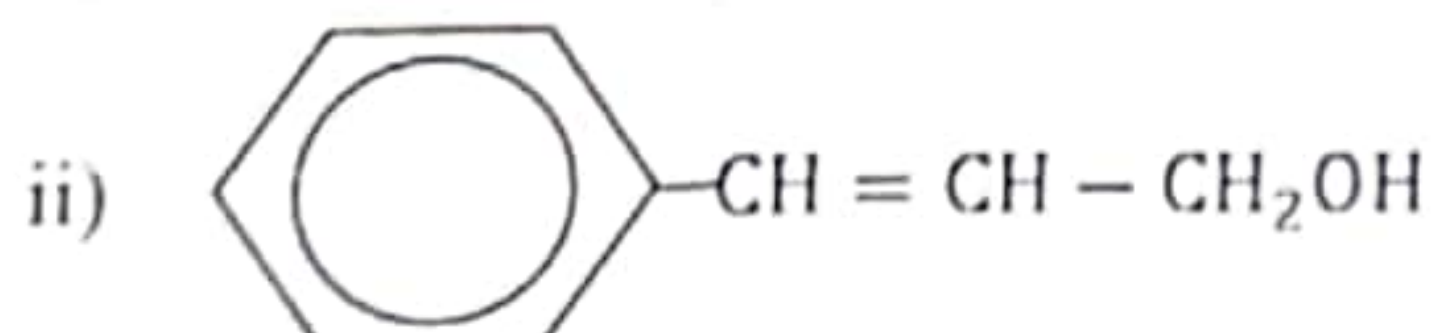
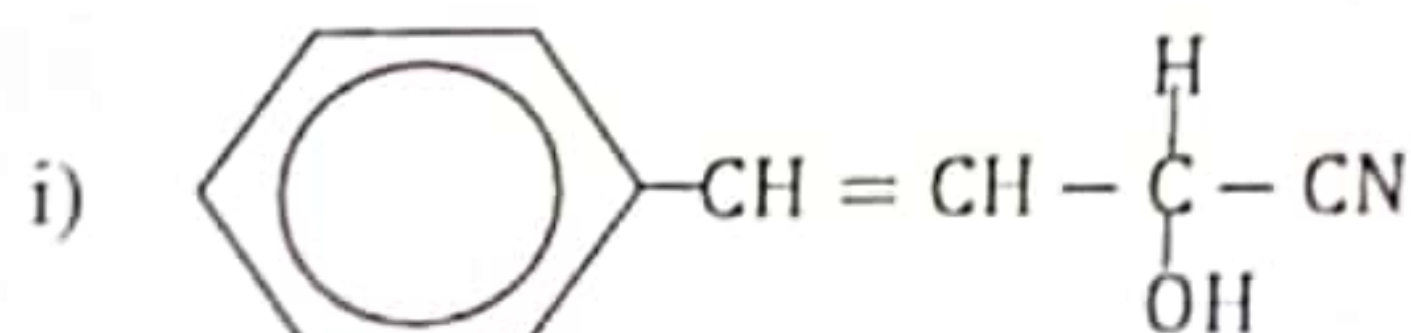
Predict the product when the following compound,



React with:

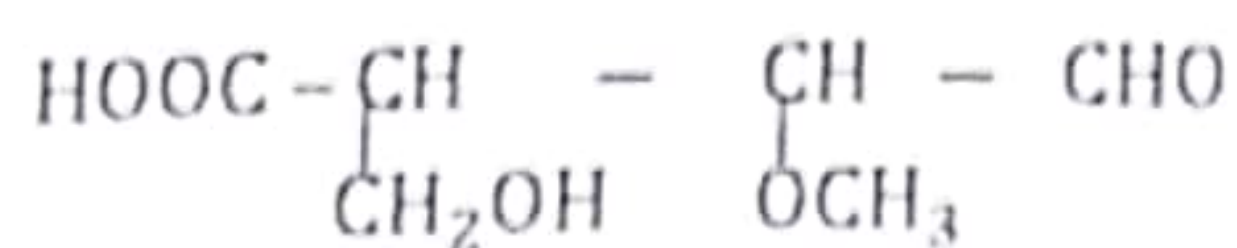
- i) Hydrogen cyanide (HCN)
- ii) LiAlH_4 in dry ether
- iii) Fehling's solution
- iv) Cold, dilute alkaline KMnO_4
- v) CH_3COCl in presence of AlCl_3

Solution



Example 3

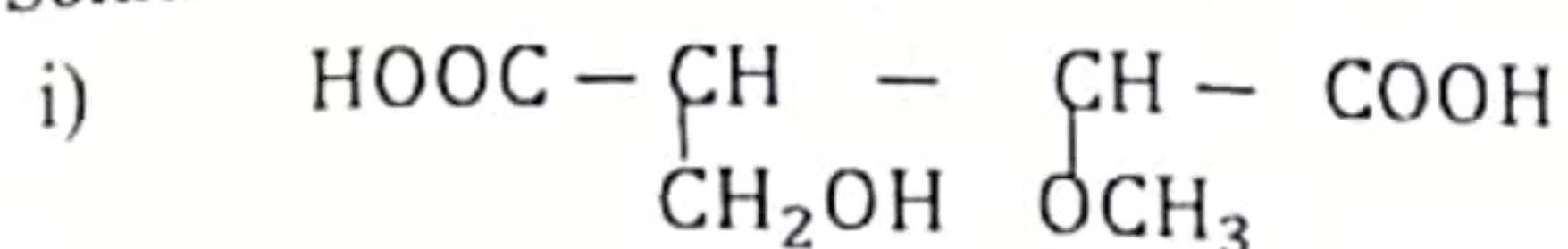
Predict the product when the following compound



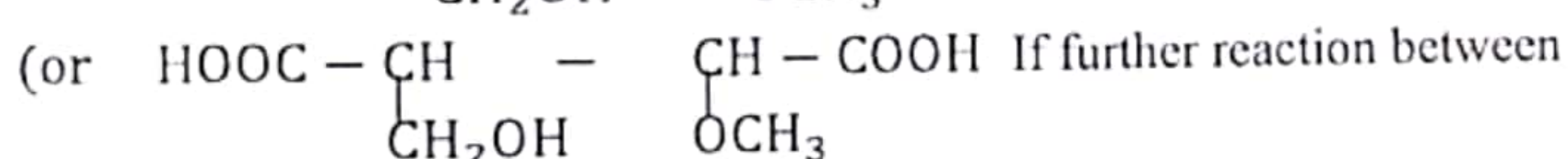
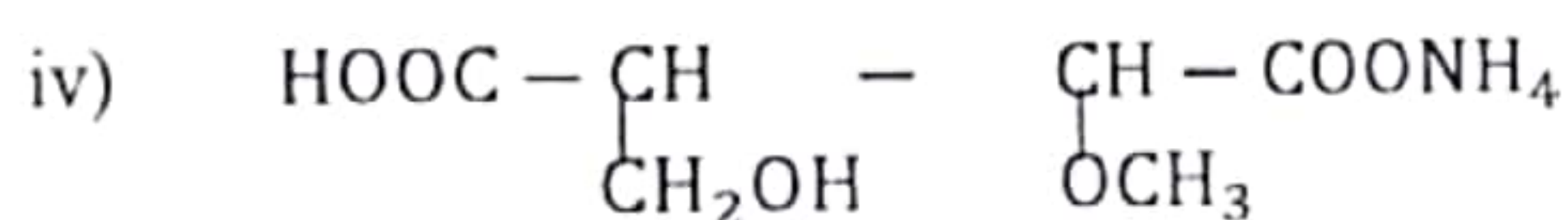
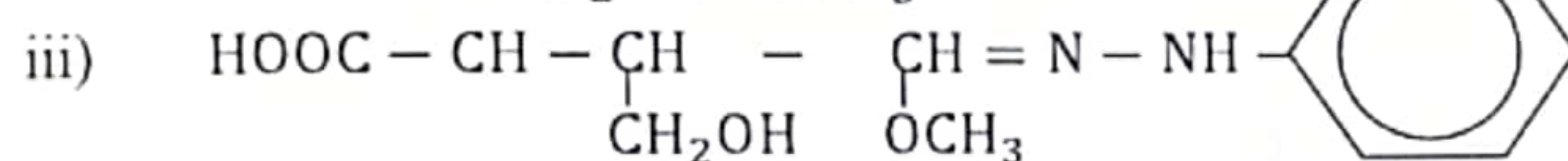
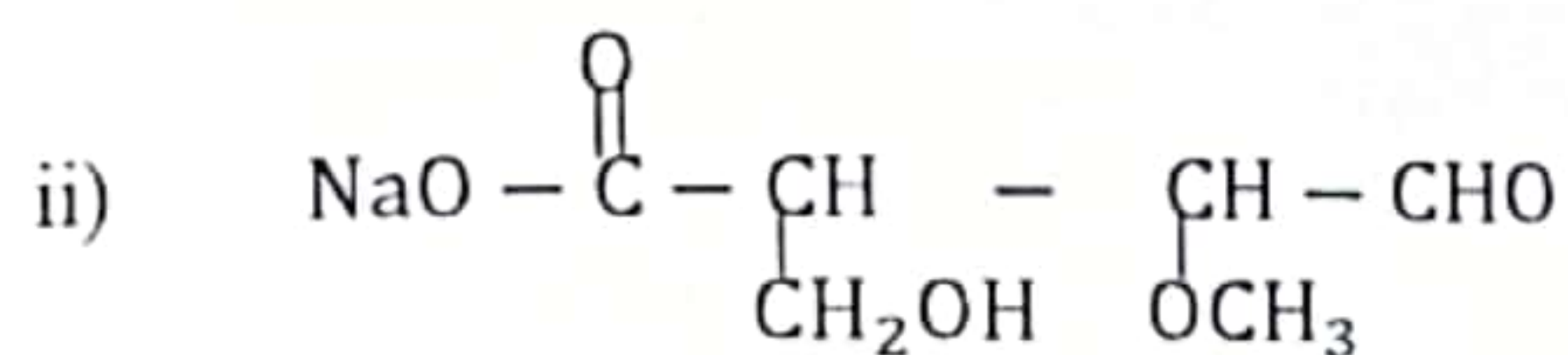
React with:

- i) Dilute KMnO_4 in presence of alkali
- ii) Dilute solution of Na_2CO_3
- iii) Phenylhydrazine
- iv) Tollen's reagent
- v) Phosphorus pentachloride

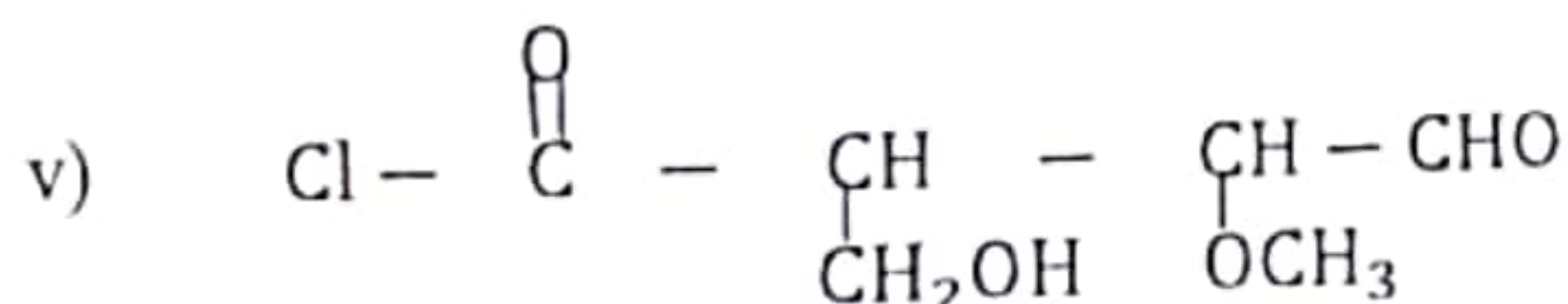
Solution



Dilute (small amount of) KMnO_4 in alkaline medium has very small oxidizing power, so only aldehyde group will be oxidised to carboxylic acid leaving alcohol group unchanged keeping in the mind the alcohol is weaker reducing agent than alcohol.



The produced NH_3 and the carboxylic acid has not been taken into consideration)



(Note: carboxylic group $-\text{COOH}$ more reactive towards PCl_5 than both alcohol group, OH , and aldehyde group, CHO , and hence only the carboxylic portion has changed).

PRACTICE EXERCISE 24

Problem 1

Name the following organic compounds:

- i.
$$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \underset{\text{NH}_2}{\text{CH}} - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$$
- ii.
$$\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \underset{\text{OH}}{\text{CH}} - \underset{\text{NH}_2}{\text{CH}} - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$$
- iii.
$$\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \underset{\text{NH}_2}{\text{CH}} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3$$
- iv.
$$\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_2\text{OH}$$
- v.
$$\text{H} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{OH}$$

Problem 2

The following names are incorrect according to IUPAC nomenclature for each name;
Write structure of the organic compound and hence give correct name

- i. 3-hydroxy-2-oxopentanamine
- ii. 3-hydroxy-5-oxopentan-2-one
- iii. 2,5-diketohexan-3-amine
- iv. 1-carboxypropanal

Problem 3

Write chemical equation to show chemical reaction of $\text{H}_2\text{N} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2\text{OH}$ with:

- i. Small amount of HCl
- ii. Excess HCl
- iii. SOCl_2
- iv. Chlorine water
- v. Chloroform under presence of KOH

Chapter 25

CONVERSIONS OF ORGANIC COMPOUNDS

Problems involving conversions may be grouped into several categories with respective methods to be applied.

But for good understanding of the methods, a reader should be so familiar with organic reactions as well as methods of preparations of different organic compounds. These provide basis of attacking conversions problems

So the organic reactions and methods of preparation of organic compounds should be very close to your mind; that is they should not be remembered by difficulty.

TYPE 1: CONVERSIONS WHICH INCREASE NUMBER OF CARBONS

This can further be divided into conversions which:

- a) Increase number of carbon by one
- b) Double number of carbons
- c) Increase number of carbons from n to $2n - 1$
- d) Increase number of carbons as you wish to any extent

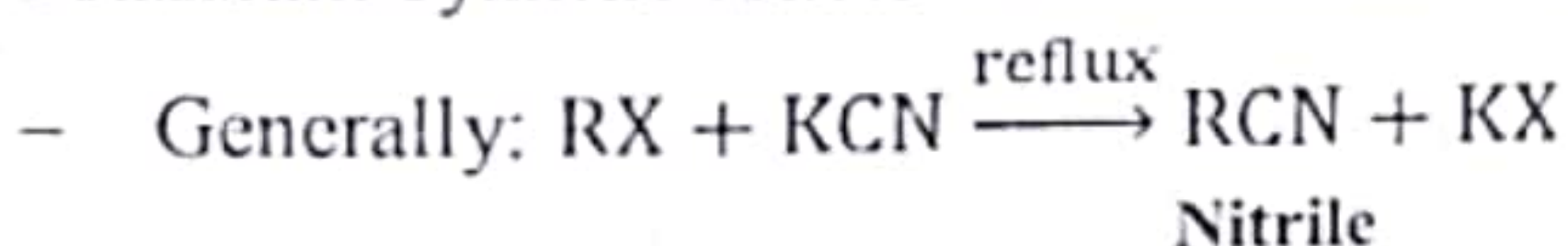
Increase number of carbon by one

This can be done by using

- (i) Potassium cyanide(KCN)
- (ii) Formation of calcium ethanoate
- (iii) Methyl magnesium halide (CH_3MgX) where X is halogen

(i) Potassium cyanide

Potassium cyanide reacts with haloalkane under reflux, yielding nitrile



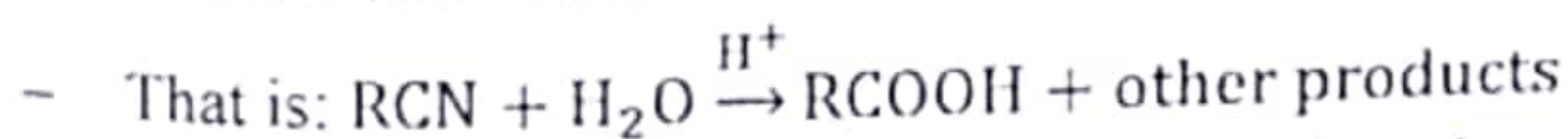
So from above general equation for the reaction, it is clearly understood that alkanitrile (organic product which is formed) has more one carbon than the original organic compound (haloalkane).

- Alkanitrile formed in above reaction is very useful in synthesis of different classes of organic compounds. It can further be converted into:

- a) Carboxylic acids
- b) Aldehydes
- c) Amines
- d) Amides

a. Alkanitrile into carboxylic acids

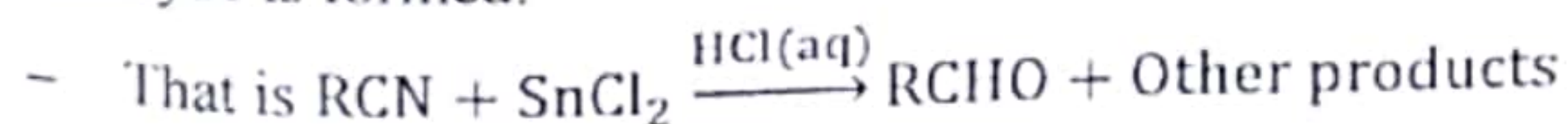
When alkanitrile is treated with acidic water, that is water with acid; carboxylic acid is formed



From the reaction equation, H^+ is from mineral acids like HCl , HNO_3 and H_2SO_4 and since H^+ combine with H_2O to form H_3O^+ , the hydronium ion (H_3O^+) is always written instead.

b. Alkanitrile into aldehyde

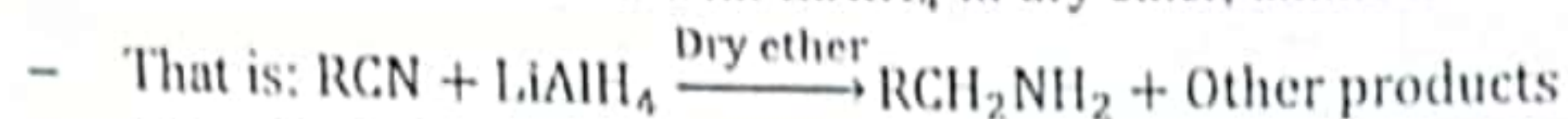
When alkanitrile is treated with tin chloride in the presence of aqueous solution of hydrochloric acid, aldehyde is formed.



The reader may wonder where oxygen atom in alkanal (aldehyde) has come from! It is not surprising as you think! The word aqueous (from aqua) means water, H_2O (aq HCl is the solution of HCl in H_2O). So the presence of water is clear explanation of the source of oxygen atom.

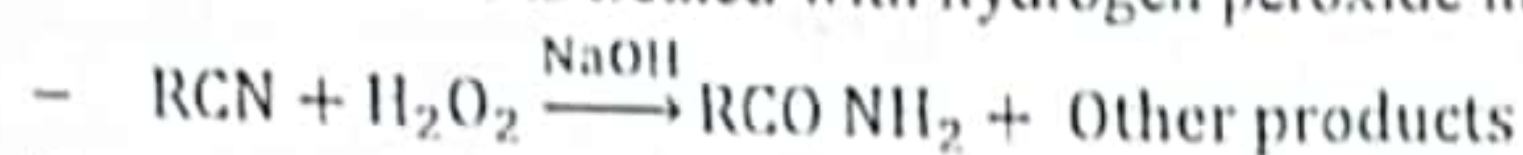
c. Alkanitrile into amines

When alkanitrile is treated with $LiAlH_4$ in dry ether, amine is formed.

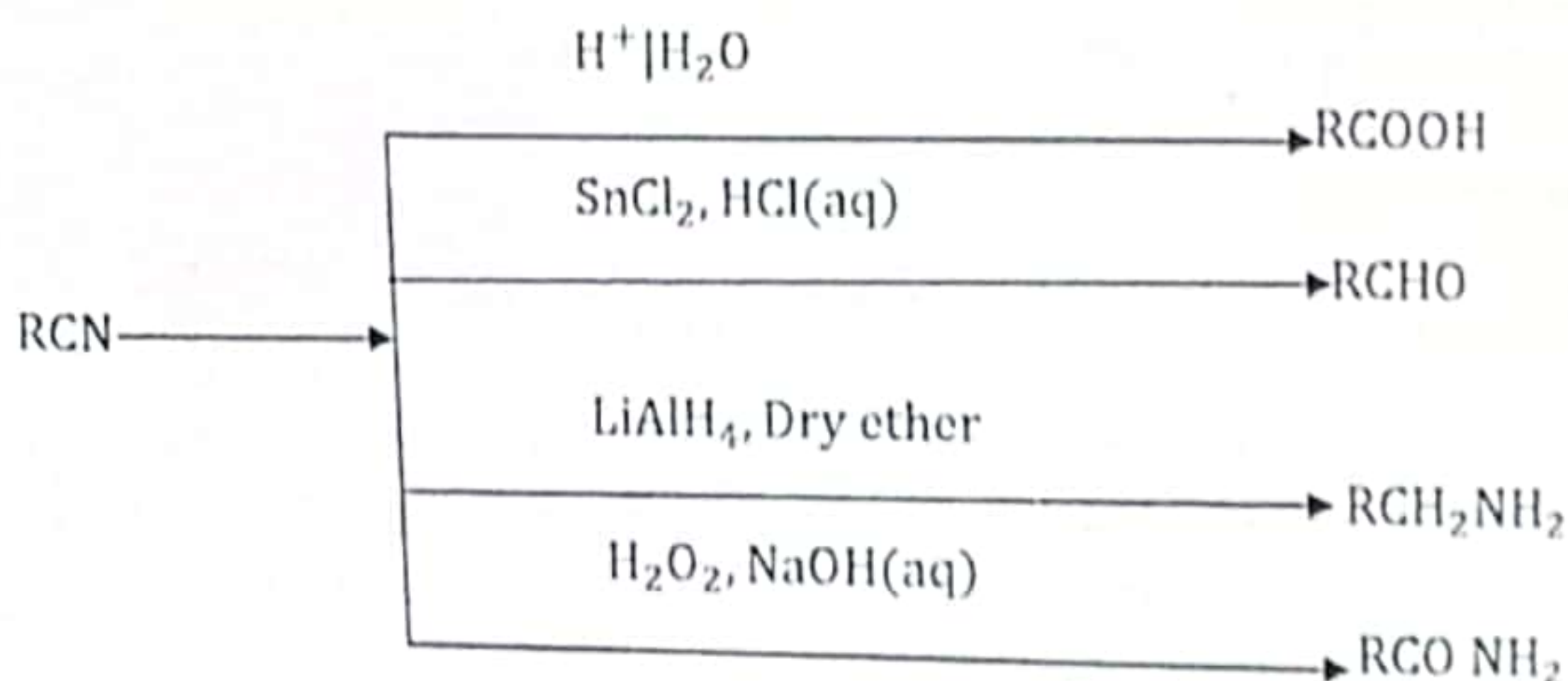


d. Alkanitrile into amide

When alkanitrile is treated with hydrogen peroxide in presence of sodium hydroxide, amide is formed.



Summary of synthesis by RCN

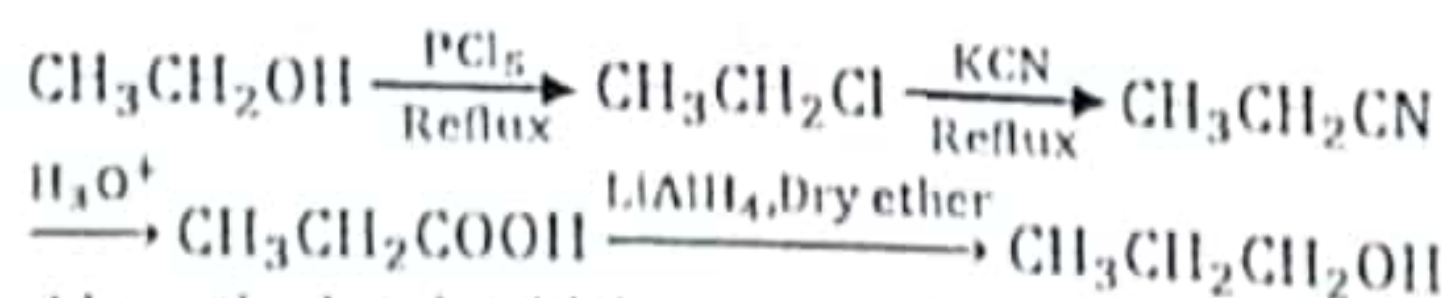


So the reader will recognise the importance of RCN in dealing with conversion problems as the products can also be converted to other organic compounds.

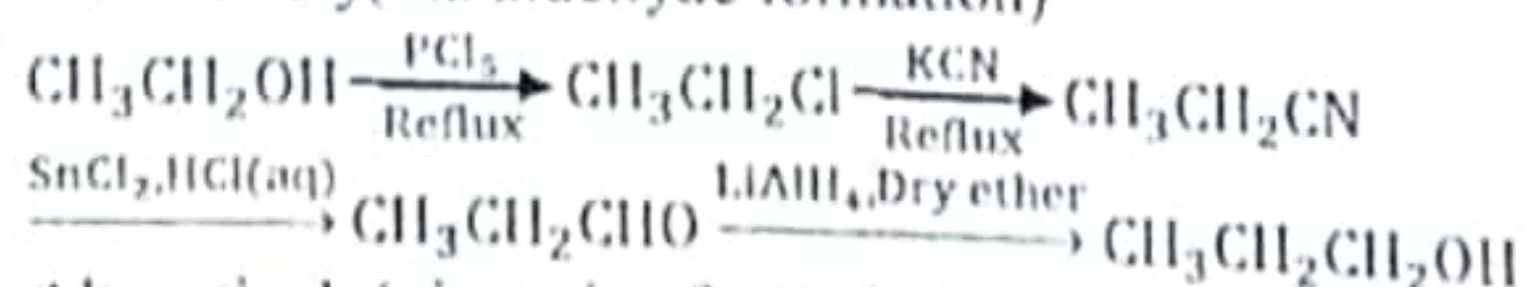
Example 1

Convert ethanol into propanol

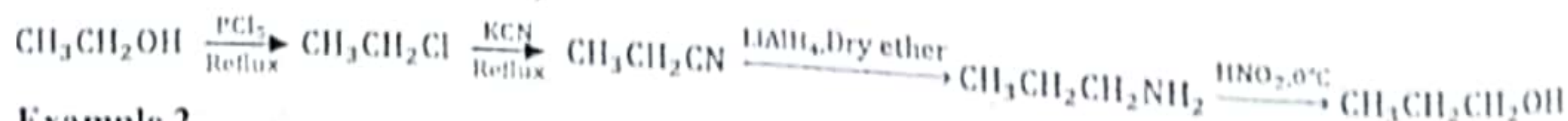
Solution



Alternatively (via aldehyde formation)



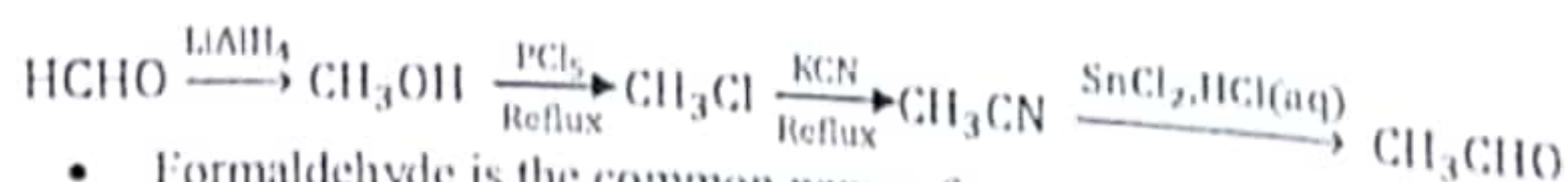
Alternatively (via amine formation)



Example 2

Convert formaldehyde into acetaldehyde

Solution

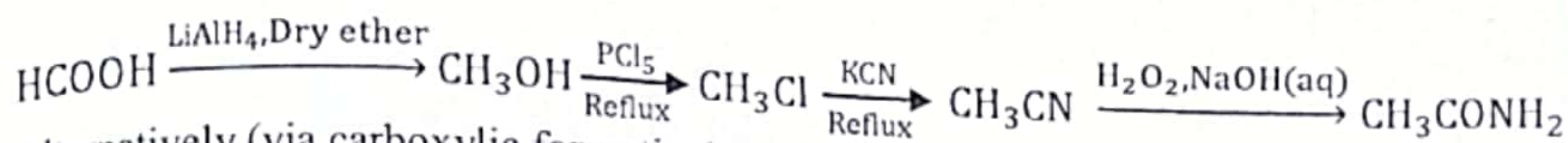


- Formaldehyde is the common name of methanol
- Acetaldehyde is the common name of ethanol

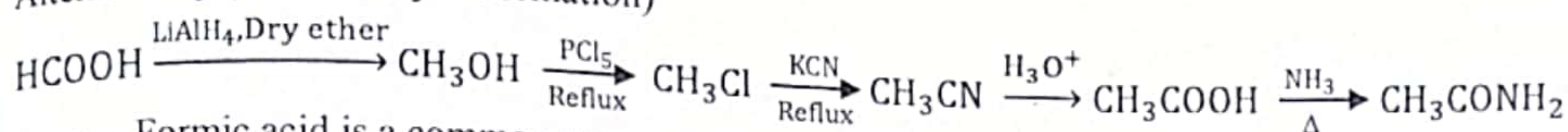
Example 3

Convert formic acid into acetamide

Solution



Alternatively (via carboxylic formation)

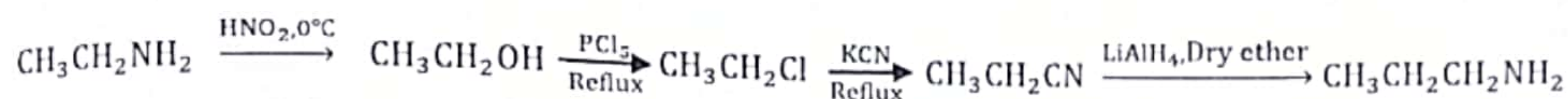


- Formic acid is a common name of methanoic acid
- Acetamide is the common name of ethanamide

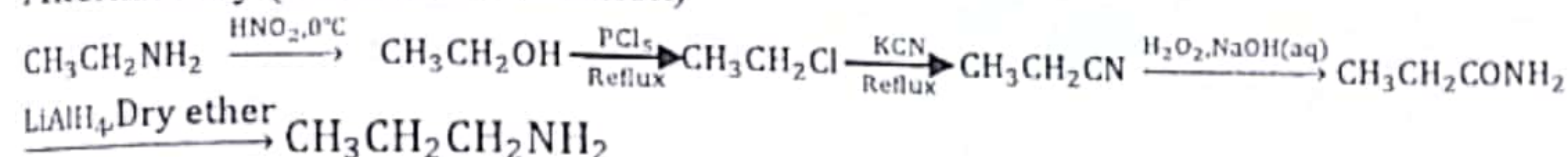
Example 4

Convert ethylamine into propyl amine

Solution

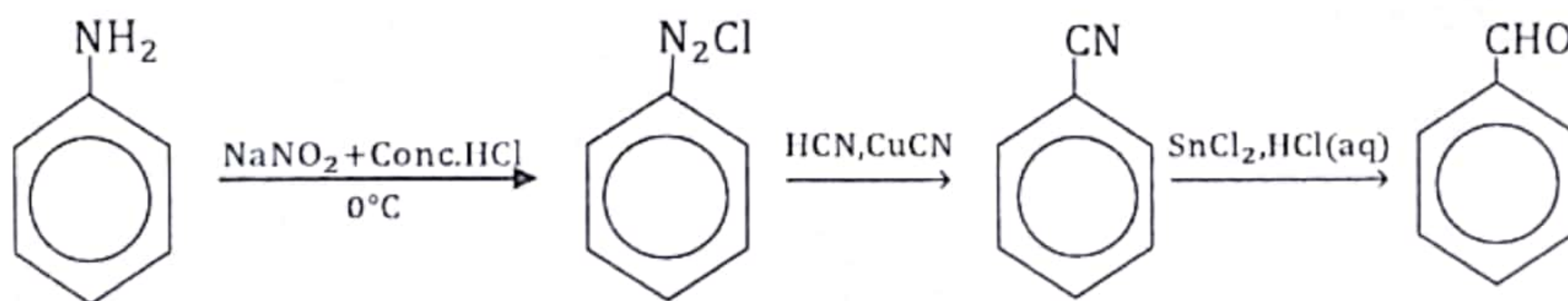


Alternatively (via amide formation)



Example 5

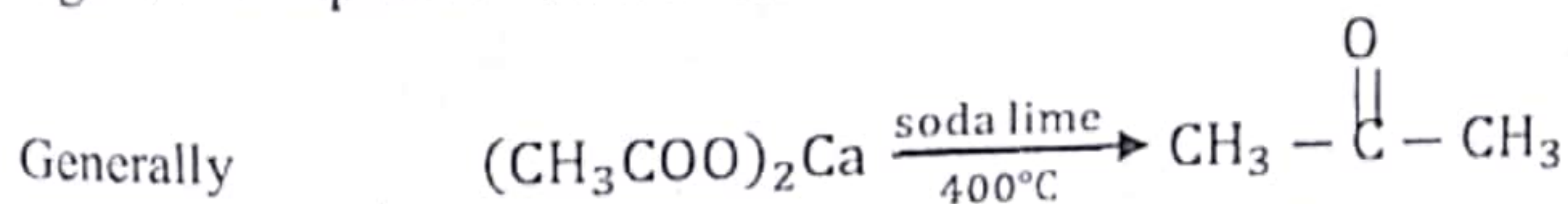
Convert aniline into benzaldehyde



- Aniline is the common name of Benzamine
- Benzaldehyde is the common name of phenylmethanal

(ii) Formation of calcium ethanoate

This method is more suitable for conversion of a certain class of organic compound into another organic compound which can be obtained via ketone formation or into ketone itself.

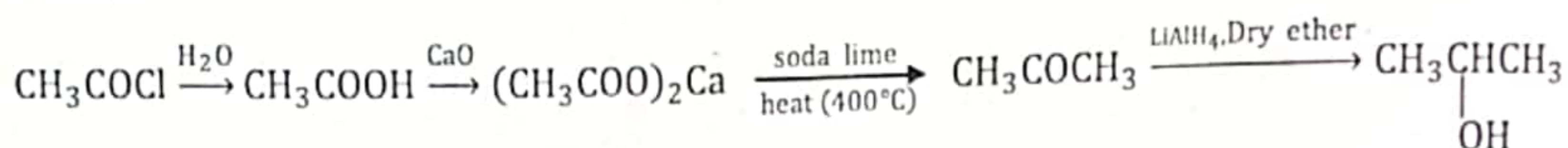


- So the method is applicable when there is possibility of converting given compound into calcium ethanoate.
- For the sake of increasing number of carbon by one, this method is **only** useful in increasing number of carbons from two to three.

Example 6

Convert acetylchloride into propan - 2 - ol

Solution

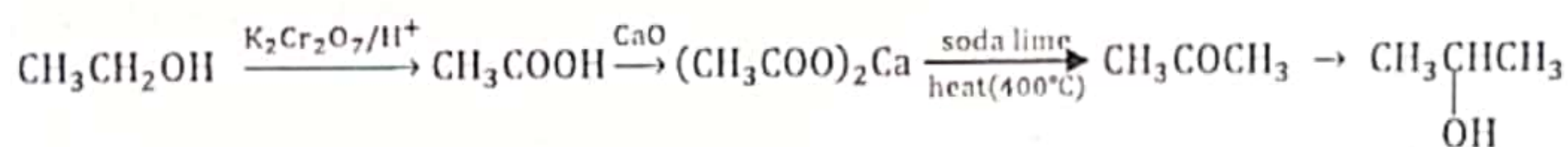


Acetyl chloride is the common name of ethanoyl chloride

Example 7

Convert ethanol into propan - 2 - ol

Solution

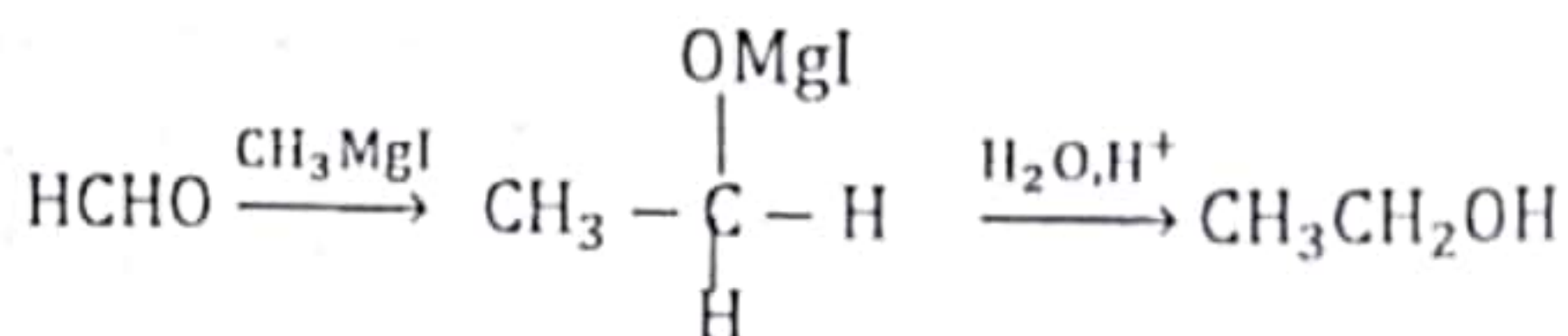


(iii) Methyl magnesium halide (CH₃MgX)

CH₃MgX can react with carbonyl compounds to form a product which can further directly converted to primary, secondary and tertiary alcohols by acidic hydrolysis.

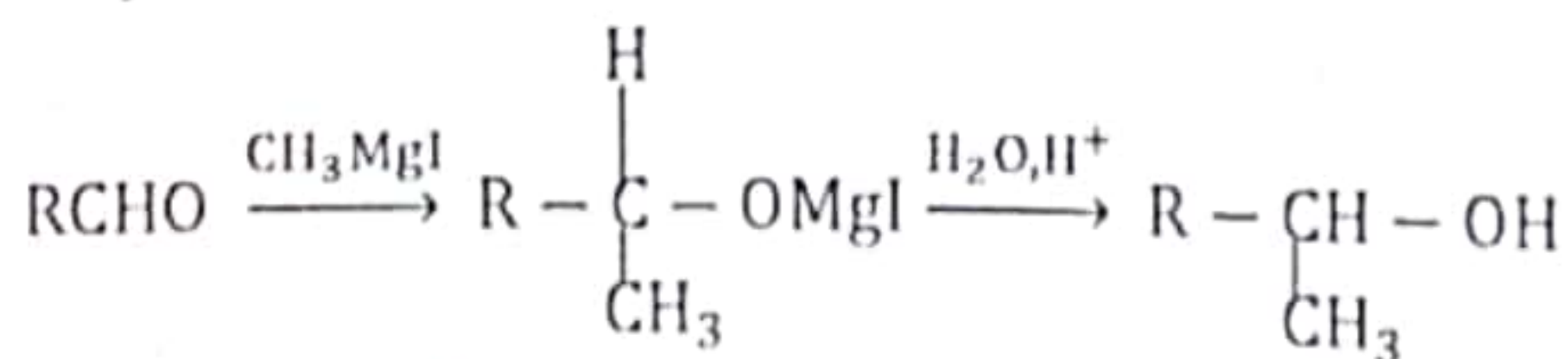
- When methanal is treated with methyl magnesium halide followed by acidic hydrolysis, ethanol is formed

That is:

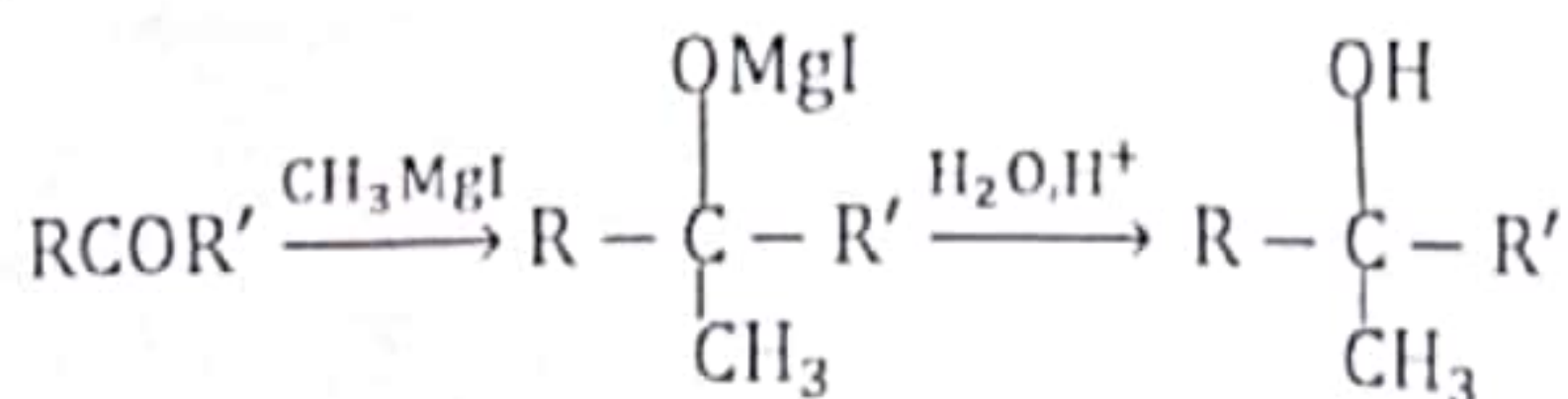


When methyl magnesium halide is treated with other aldehydes (except methanal) followed by hydrolysis secondary alcohols are formed

That is:



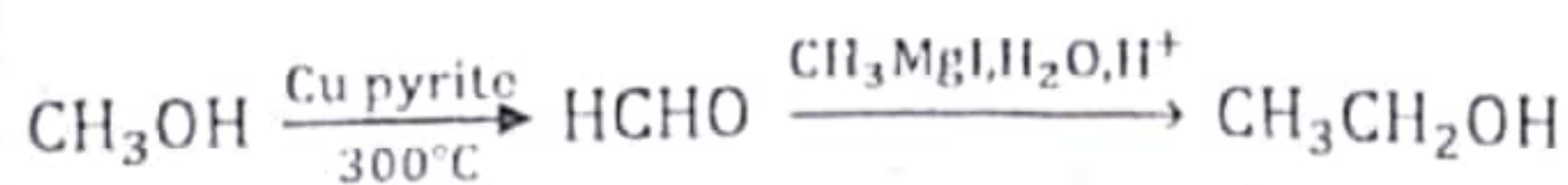
When methyl magnesium halide is treated with ketone followed by hydrolysis, tertiary alcohol is formed.



Example 8

Convert methanol into ethanol

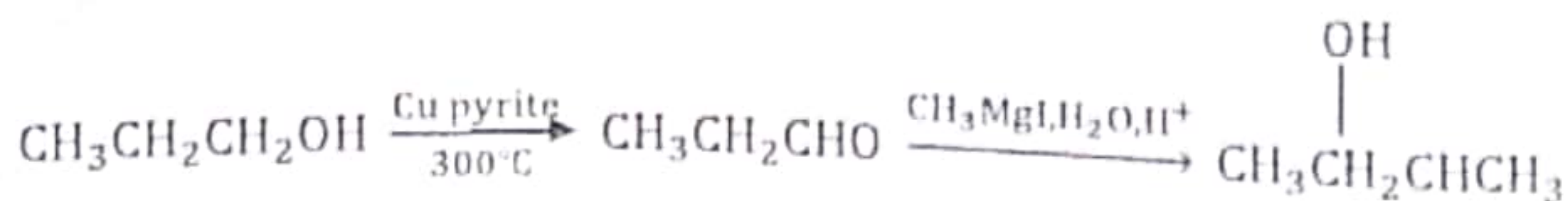
Solution



Example 09

Convert propanol into butan - 2 - ol

Solution



Explanation of the choice of the method among the three

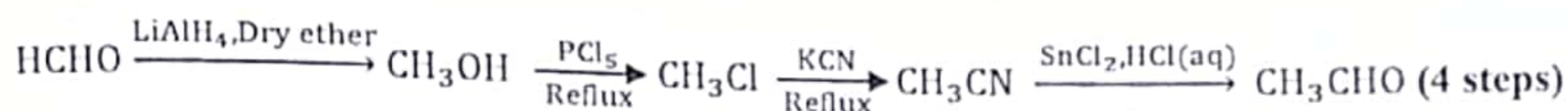
The question which remains to the reader up to now is: *if there is a need of increasing number of carbons by one; how can I recognise that I should use KCN, CH_3MgX or the formation of $(\text{CH}_3\text{COO})_2\text{Ca}$?*

– The following explanation is the answer of the above question

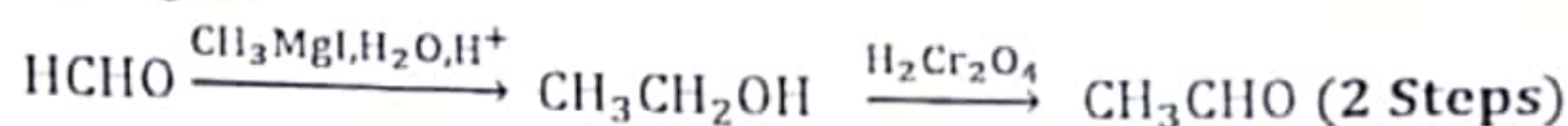
Firstly the reader will agree with me that: **the shorter method is the better method** as it consumes less time and energy. So if there is more than one method which can be applied in dealing with a given conversion, the shorter method is the one to be applied.

– For example in converting methanol into ethanal, the following methods can be applied.

1st case: by using KCN



2nd case: by using Grignard reagent



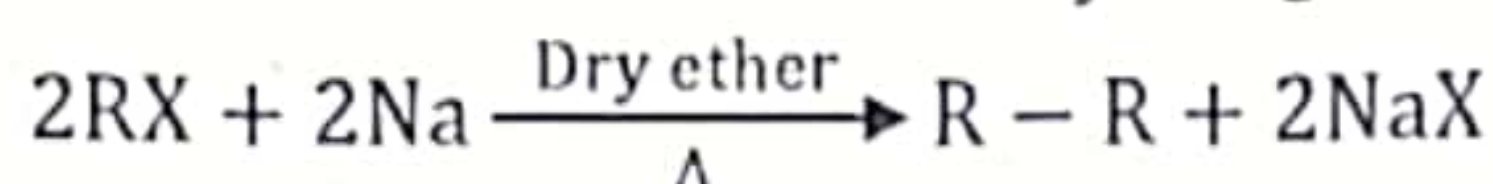
- So it is easily understood that the second method is the better method as it involves two steps only while the first one involves four steps to get the final product from the same compound.
- However, sometimes the examiner restricts number of steps to be applied by a candidate in answering conversion problem and is poor minded candidates only who will ignore instructions of examiner! So in above example if you are asked to use 4 steps, the first method is the one to be applied although it is more tedious and time consuming than the second method. So the reader should recognise the importance of understanding different methods dealing with the same conversion problem

Another factor to consider is **the structure of new product**.

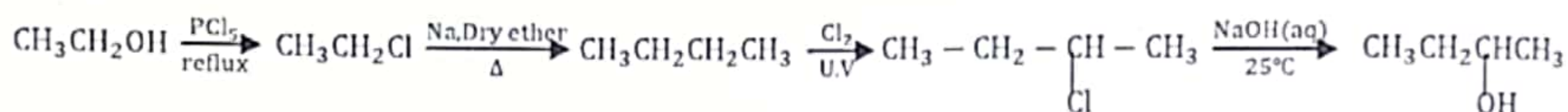
- Sometimes you will find it is too difficult to attain certain conversion by one method while it is easier to attain the same conversion by another method. To understand this consider the following cases:
- In converting propanol into butan-2-ol*
 - It's not easy to deal with above conversion using KCN or formation of calcium ethanoate (in your own try to attempt to answer the problem using KCN or formation of calcium ethanoate) but by using Grignard reagent is easier. KCN increase number of carbons but does not change class of alcohol (on reduction of carboxylic acids or aldehyde or formation of alcohol from amine).
 - In converting propanol into butanol*
 - Unlike to (i), in this case neither formation of $(\text{CH}_3\text{COO})_2\text{Ca}$ nor CH_3MgI can be applied (on your own attempt to answer the problem by using CH_3MgI or formation of $(\text{CH}_3\text{COO})_2\text{Ca}$ to justify the statement) but by using KCN the problem become easier.
 - In converting formic acid into acetamide*
 - It has been shown that amide can be prepared from nitrile by using H_2O_2 under presence of NaOH and number of carbons is increased by one. All of these implies that KCN must be applied because you cannot easily get the amide from neither CH_3MgI nor formation of $(\text{CH}_3\text{COO})_2\text{Ca}$
 - The same factors are considered in choosing a method to use in dealing with other kinds of conversions.

Doubling number of carbons

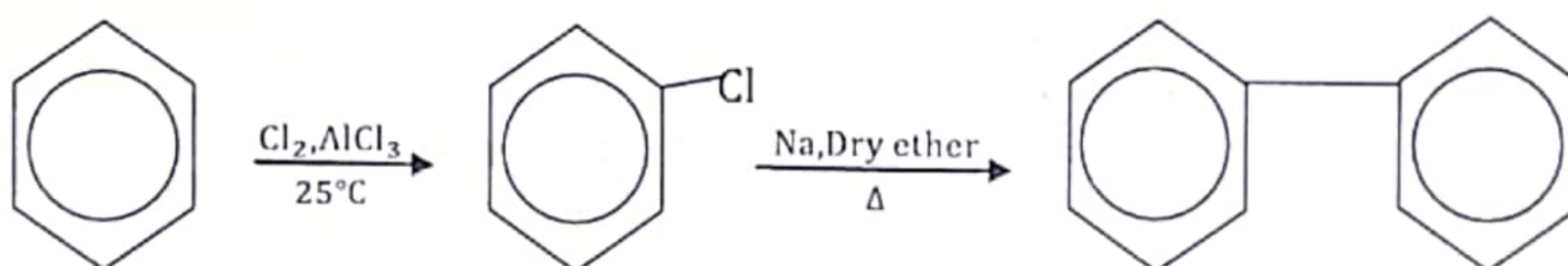
Under this heading, the most common method is by using Wurtz reaction. That is;

**Example 10**

Convert ethanol to butan - 2 - ol

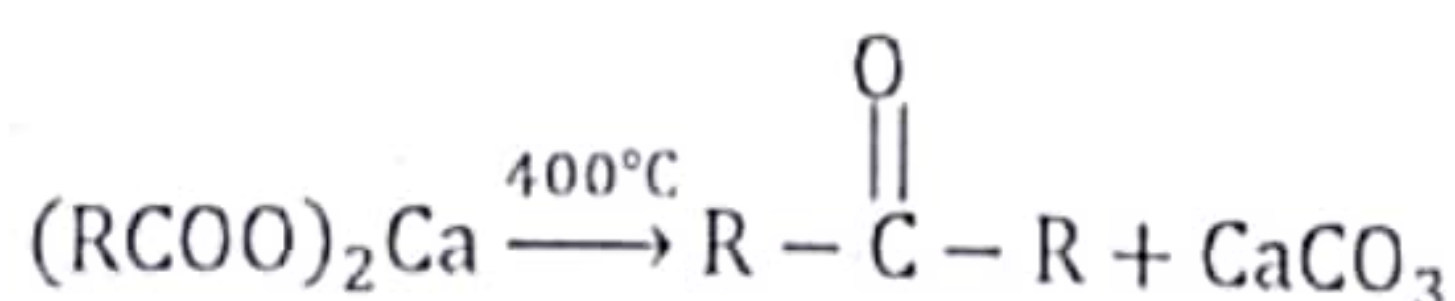
Solution**Example 11**

Convert benzene into phenylbenzene

Solution**Increasing number of carbons from n to 2n - 1**

Under this heading, conversion is dealt via formation calcium carboxylate.

Generally;



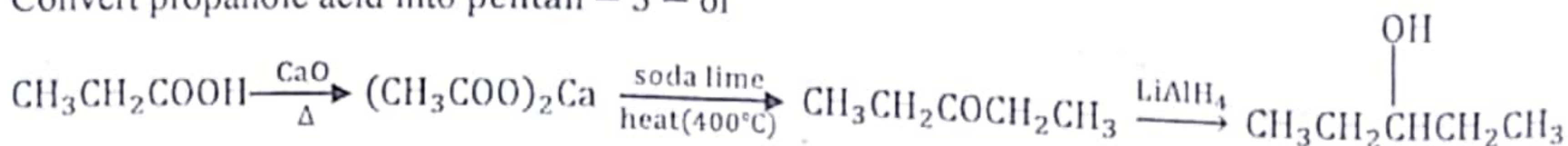
So the method is applicable if there is possibility of forming calcium carboxylate easily from given compound and the final product can be derived from ketone or is ketone itself.

Example 12

Convert propanol acid to pentan - 3 - one

Solution**Example 13**

Convert propanoic acid into pentan - 3 - ol



It should be understood that in the above two examples, original compounds have 3 carbons in each i.e n = 3 while the final compounds have $2 \times 3 - 1 = 5$ (i.e 2n - 1) carbons

Increasing number of carbons as you wish(to any extent)

This can be done by using:

- (i) Grignard reagent
- (ii) Alkylation of acetylide ion

(i) Grignard reagent

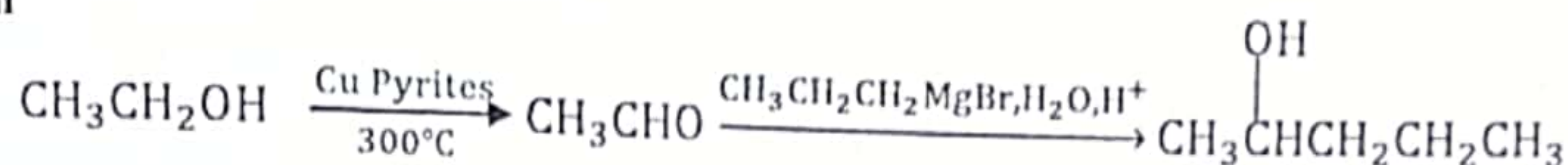
Grignard reagents have general molecular formular of $R-MgX$ where R is the alkyl group

- So number of carbons can be increased in any extent depending on the choice of alkyl group (R). If the alkyl group is methyl group, CH_3 , then number of carbons will be increased by one. If the alkyl group is ethyl group, CH_3CH_2 then number of carbons will be increased by two and so on.
- Thus the reader should recognise that the use of methyl magnesium halide, CH_3MgX is the special case of this method where by number of carbons is increased by one.

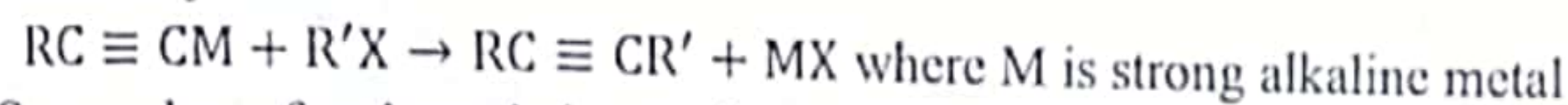
Example 14

Convert ethanol to pentan - 2 - ol

Solution

**(ii) Alkylation of acetylide ion**

Generally;

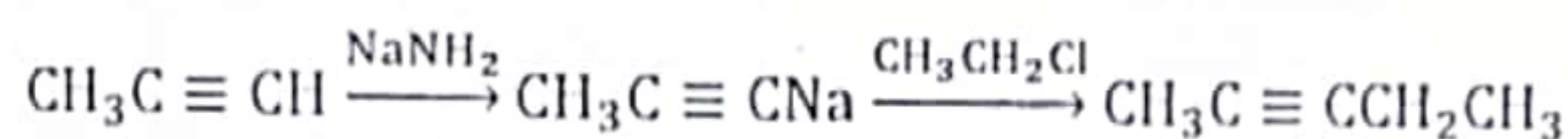


So number of carbons is increasing depending on the choice of alkyl group(R)

Example 15

Convert propyne into pent - 2 - yne

Solution



In the above conversion we have used chloroethane, $\text{CH}_3\text{CH}_2\text{Cl}$ for purpose of increasing two carbons according to the question. If the question asks to increase one carbon only chloromethane, CH_3Cl should be used, three carbons chloropropane is used and so on.

TYPE 2: CONVERSIONS WHICH DECREASE NUMBER OF CARBONS

This can further divided into conversions which:

- Decrease number of carbons by one
- Decrease number of carbons to any extent

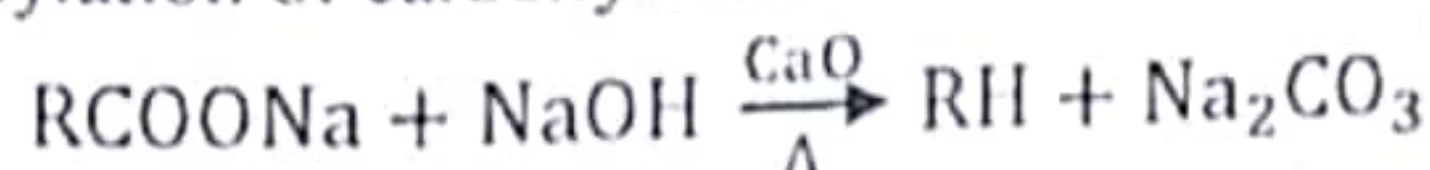
Decrease number of carbons by one

For this purpose, the following methods are commonly applied:

- Decarboxylation of carboxylic salts
- Hoffmann degradation reaction

(i) Decarboxylation of carboxylic salts

Decarboxylation of carboxylic salts leads to formation of alkane according to the following equation:

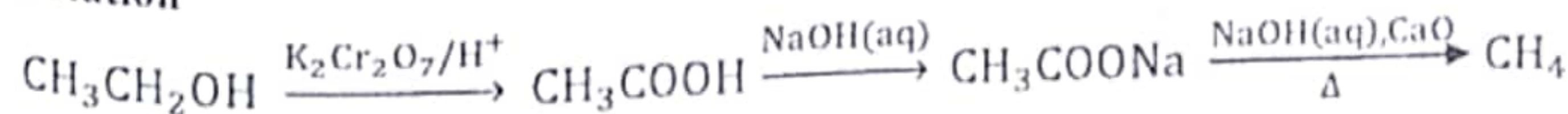


Where RCOONa has $n + 1$ carbons (R with molecular formular $\text{C}_n\text{H}_{2n+1}$ has n carbons and COONa has 1 carbon making a total of $n + 1$ carbons in RCOONa) while in RH (alkane) there are n carbons. Thus number of carbons has decreased from $n + 1$ to n .

Example 16

Convert ethanol into methane

Solution

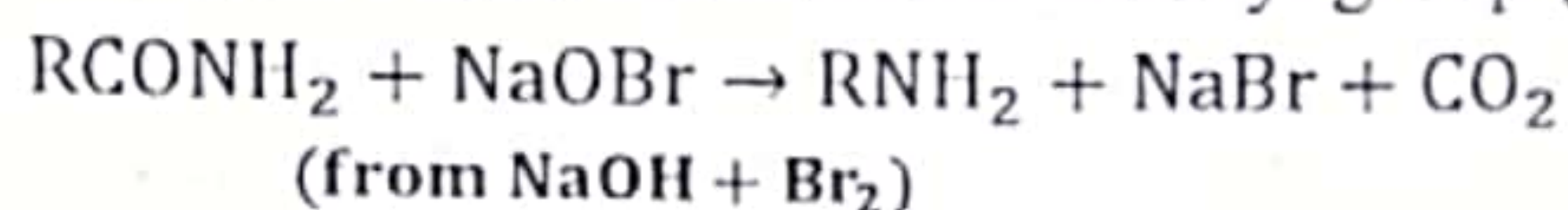


Example 17

Convert toluene into chlorobenzene

Solution

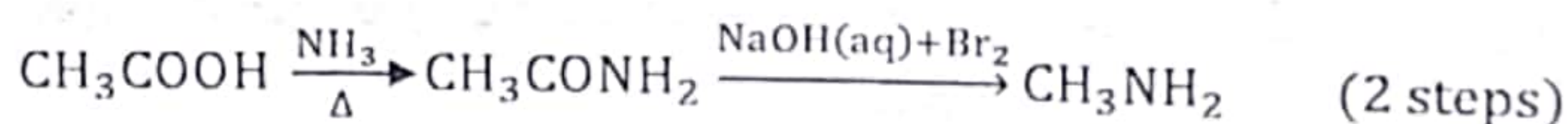
(ii) Hoffmann degradation

 In this reaction there is elimination of carbonyl group ($-\text{CO}$) from amide to form amine.

 Thus number of carbons has decreased from $n+1$ in RCONH_2 to n in RNH_2

- The method is applicable when original compound to be converted is either amide or can be converted easily to amide before attaining required conversion

Example 18

Convert acetic acid into methyl amine

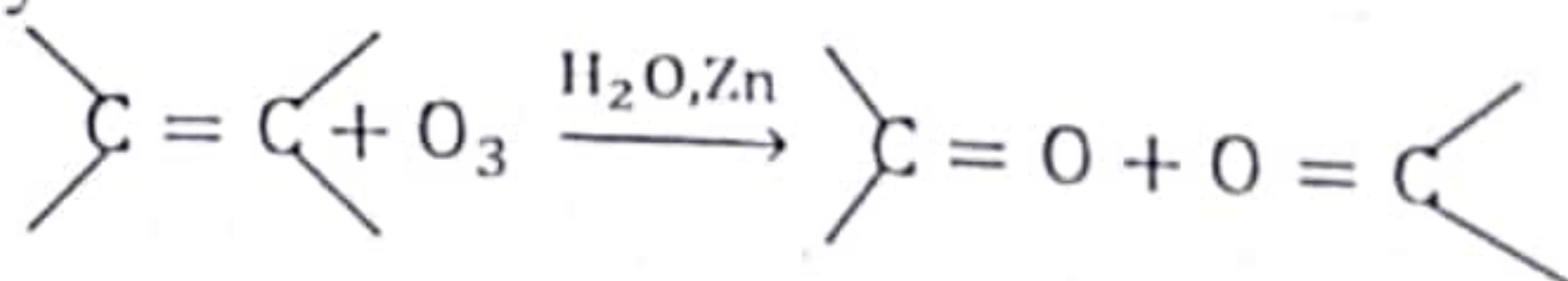
Solution


Alternatively

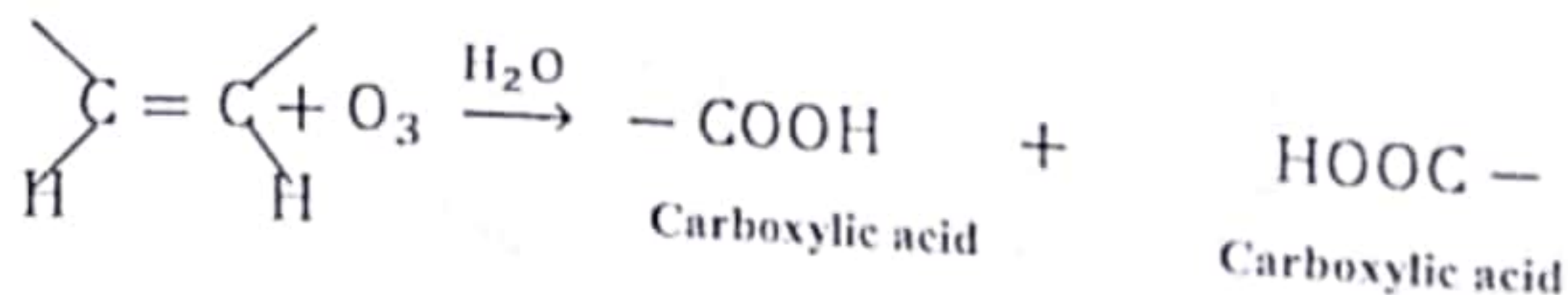

Decrease number of carbons to any extent

The method which is commonly used for this purpose is ozonolysis.

Generally



Or (If Zn is absent)


Example 19

Convert butan-2-ol into ethanoic acid

Solution


Formation of but-2-ene and not but-1-ene in above reaction is according to **Saytzeff's rule** which states that 'Alkene with greater number of alkyl groups at double bond is more stable'

TYPE 3: CONVERSIONS WHICH INVOLVE THE CHANGE OF SUBSTITUENT OR FUNCTION GROUP

This can be subdivided into:

- The change of position of the same substituent (or functional) group
- The introduction of new substituent (or functional) group

The change of position of the same substituent (or functional) group

This can further be divided into:

- (i) *Conversions which do not involve the change of number of carbons for aliphatic organic compound*

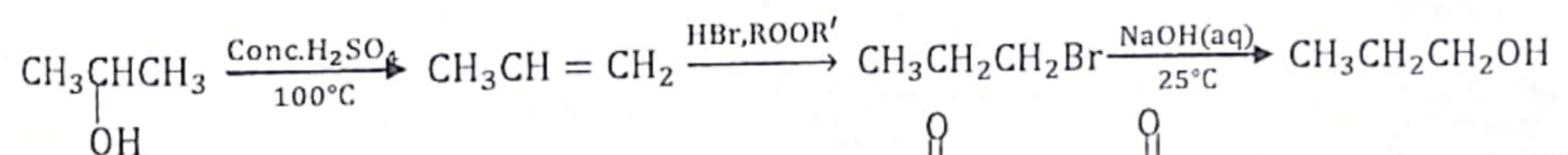
In this case, the technique is to change the given organic compound to alkene then the required product found by either Markownikoff's or Anti-Markownikoff's addition.

- It should be noted that only HBr in presence of organic peroxide undergo Anti-Markownikoff's addition.

Example 20

Convert propan-2-ol into propanol

Solution

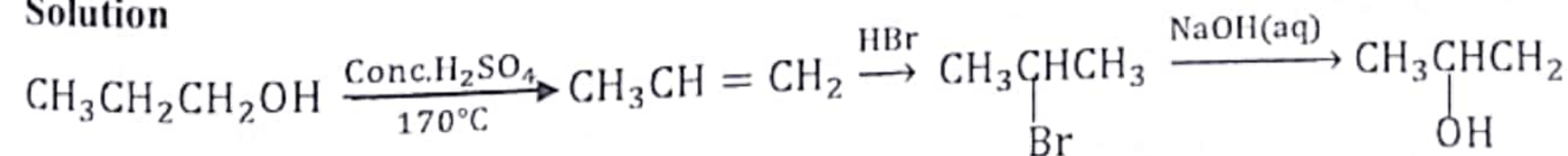


Examples of organic peroxide are ROOR' and $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$ where R and R' are alkyl or aryl groups

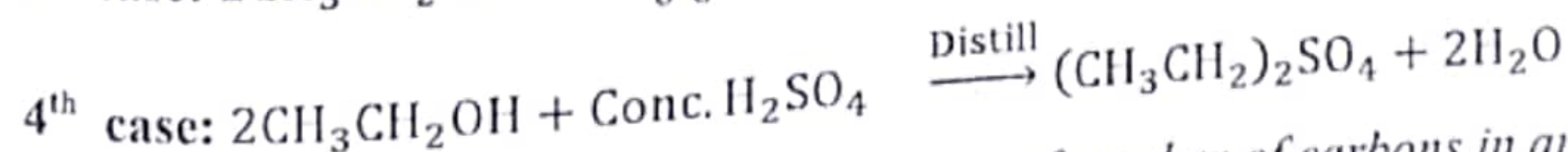
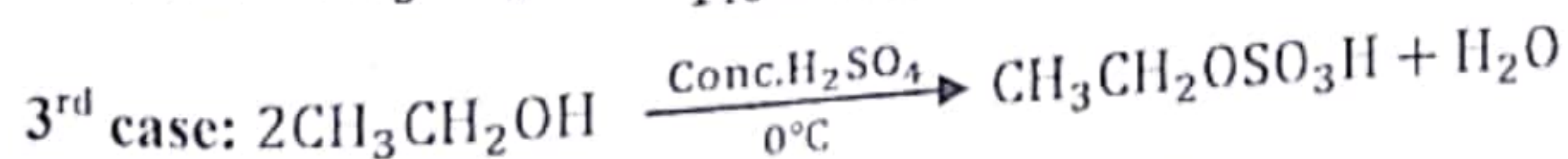
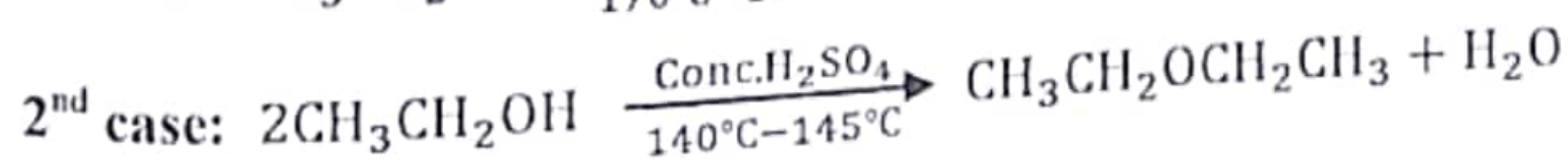
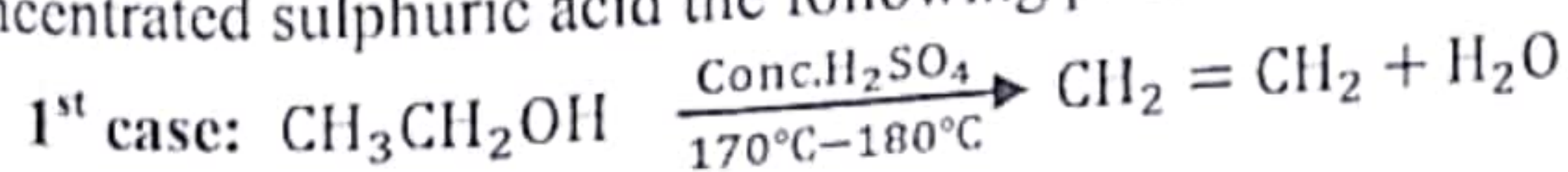
Example 21

Convert propanol into propan-2-ol

Solution



It is very important to indicate the reliable temperature to be applied in above reaction (dehydration of alcohol by conc. H₂SO₄) as the reaction between alcohol and concentrated sulphuric acid is the one of reactions which are very sensitive to temperature change. Once the temperature is changed the new organic product (or mixture of organic) is formed e.g. for reaction between ethanol and concentrated sulphuric acid the following products can be formed at different temperature.



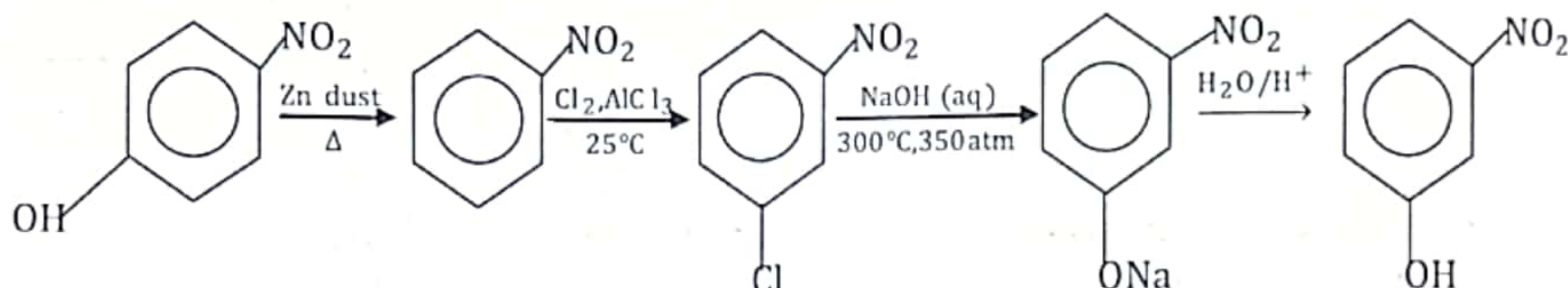
- (ii) *Conversions which do not involve the change of number of carbons in aromatic compounds*
- In this case the technique is to understand what substituent group is to be removed firstly and then return it again to benzene ring. The choice depends on the relation of substituent groups in new product.

- If are ortho or para related, the ortho-para director should not be removed and the meta director is one to be removed before returning again to benzene ring.
- If are meta related, the meta director should not be removed and ortho-para director is the one to be removed before returning again to benzene ring

Example 22

Convert p-nitrophenol into m-nitrophenol

Solution

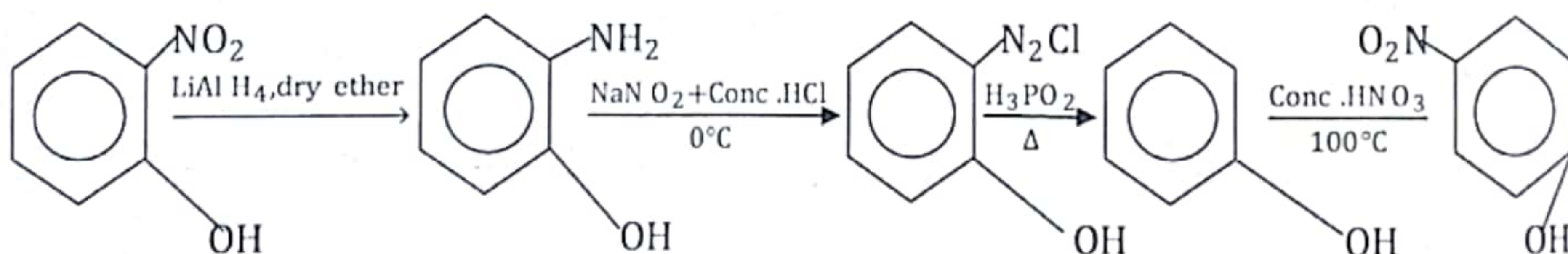


P stands for para. So p-nitrophenol implies that NO_2 (nitro) and OH in phenol are para related. Similarly for m-nitrophenol, where m stands for meta

Example 23

Convert o-nitrophenol into p-nitrophenol

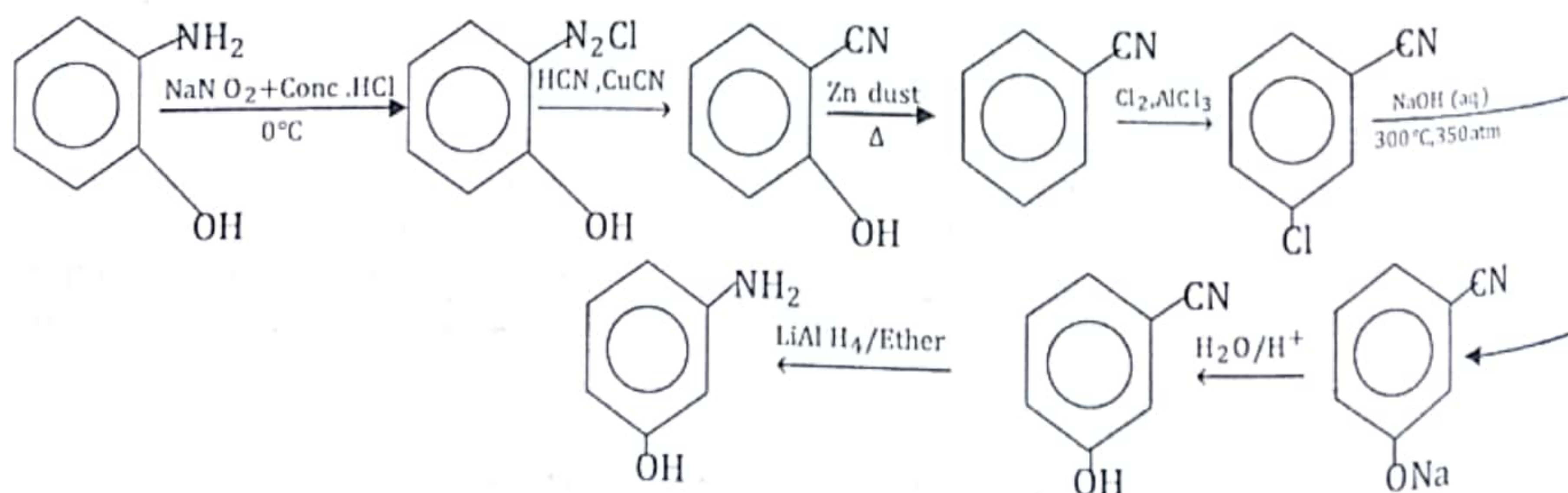
Solution



Example 24

Convert o-aminophenol into m-aminophenol

Solution



The difficulty of this question was to find an intermediate meta-director from either NH_2 or OH and the intermediate must be capable of being reconverted to NH_2 or OH respectively.

Example 25

Convert o-aminophenol into p-aminophenol

Conversions which increase m.p.

The choice of Grignard reagent depends on the number of carbons which is increased. If there is an increase in number of carbons by one, methyl magnesium halide is used, If there is an increase in number of carbons by two, ethylmagnesium halide is used; and so on.

Convert propanol into butan - 2 - ol

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[300^\circ\text{C}]{\text{Cu pyrite}} \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{\text{CH}_3\text{MgBr}, \text{H}_2\text{O}/\text{H}^+} \text{CH}_3\text{CH}_2\overset{\text{OH}}{\text{CH}}\text{CH}_3$$

Convert 1 – chloropropane into 3 – chloropentane

Solution

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow[25^\circ\text{C}]{\text{NaOH(aq)}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[300^\circ\text{C}]{\text{Cu pyrite}} \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow[\text{H}_2\text{O/H}^+]{\text{CH}_3\text{CH}_2\text{MgBr}} \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3 \xrightarrow{\text{PCl}_5} \text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$$

THE INTRODUCTION OF NEW SUBSTITUENT (OR FUNCTIONAL) GROUP

- (i) Aliphatic organic compound
- (ii) Aromatic organic compound

If the conversion involves an interchange of two halogens, the special attention must be kept. The displacement of one halogen by another depends on the strength of nucleophile which follows following order:



Least nucleophilic

Convert chloroethane into iodoethane

$$\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{KI}} \text{CH}_3\text{CH}_2\text{I}$$

Chloroethane from iodoethane cannot simply prepared in that way since Cl^- is less nucleophile than I^- thus making incapable for it to displace I from iodoethane.

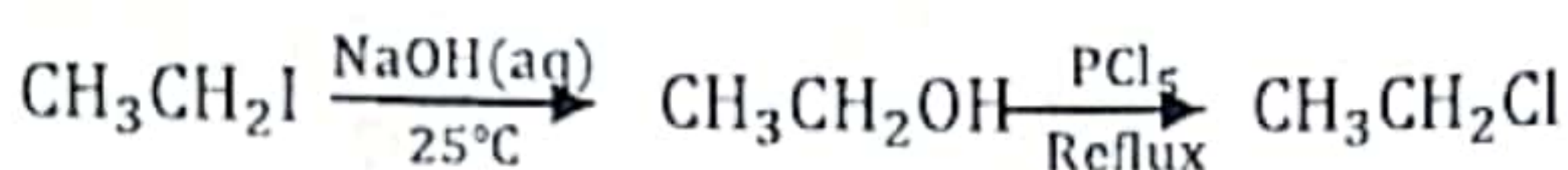
i.e. $\text{CH}_3\text{CH}_2\text{I} + \text{KCl} \rightarrow \text{No reaction}$

Let us see how it's done in next example!

Example 29

Convert $\text{CH}_3\text{CH}_2\text{I}$ into $\text{CH}_3\text{CH}_2\text{Cl}$

Solution



(ii) *In aromatic organic compound*

If there is only one substituent in new product after conversion, the case is easier

BUT

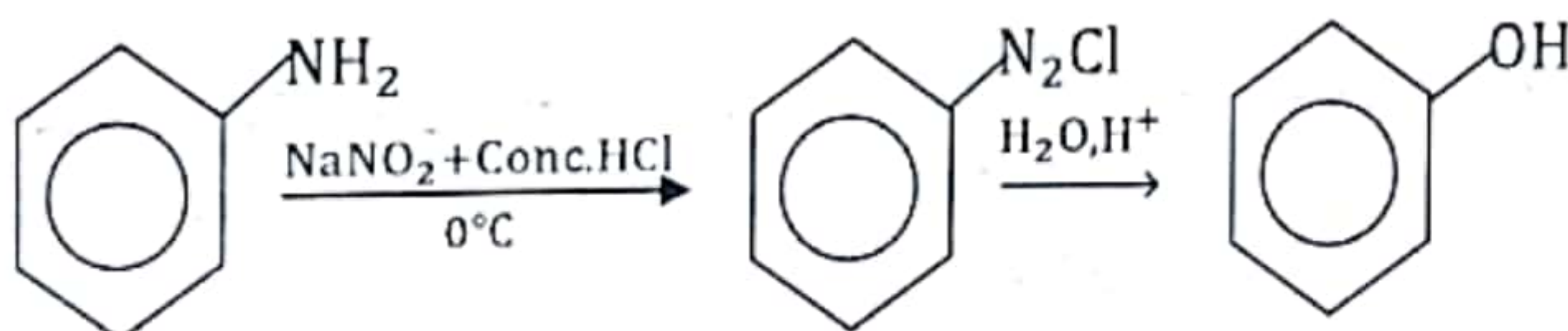
If it involves more than one substituent in benzene ring, needs a special attention.

- If two substituents are para related, the ortho-para director which form para product as major product (in all ortho-para directors except halogens) must be entered first. But if two substituents have same effect (Both form para product as major product) either of the two may be entered first.
- If two substituents are ortho-related, halogens which are only ortho-para directors forming ortho product as the major product must be entered first.
- If two substituents are meta-related, meta director must be entered first. But if all of the two substituents are meta directors, anyone can be entered first.

Example 30

Convert aniline into phenol

Solution

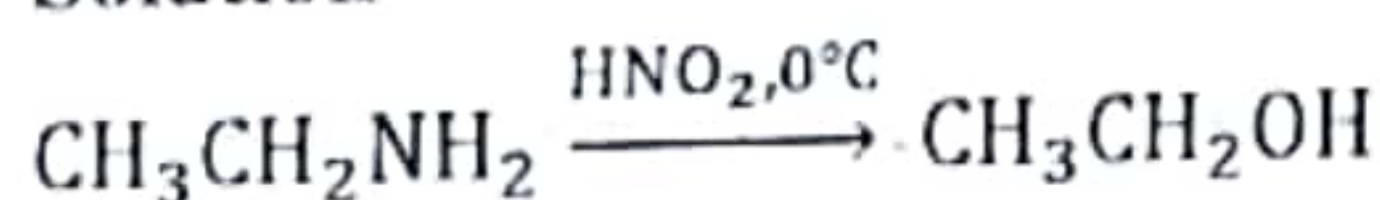


The use of mixture of NaNO_2 and Conc. HCl is to prepare HNO_2 (nitrous acid) which leads to **diazotisation** of aniline.

Example 31

Convert $\text{CH}_3\text{CH}_2\text{NH}_2$ into $\text{CH}_3\text{CH}_2\text{OH}$

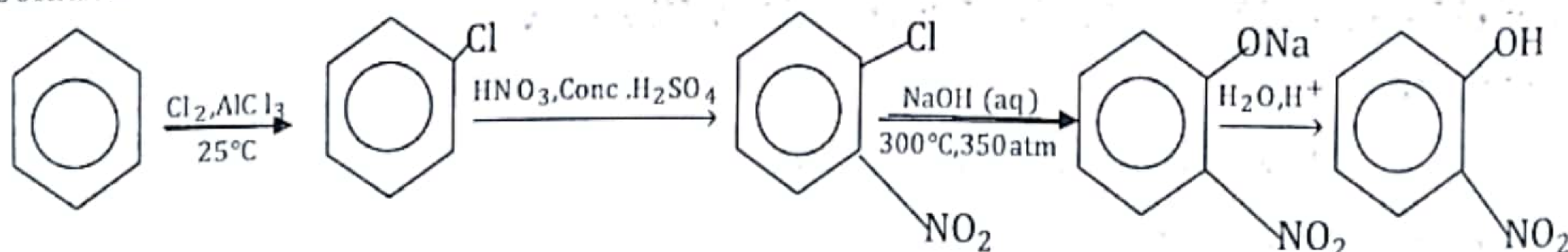
Solution



Example 32

Convert benzene into o-nitrophenol

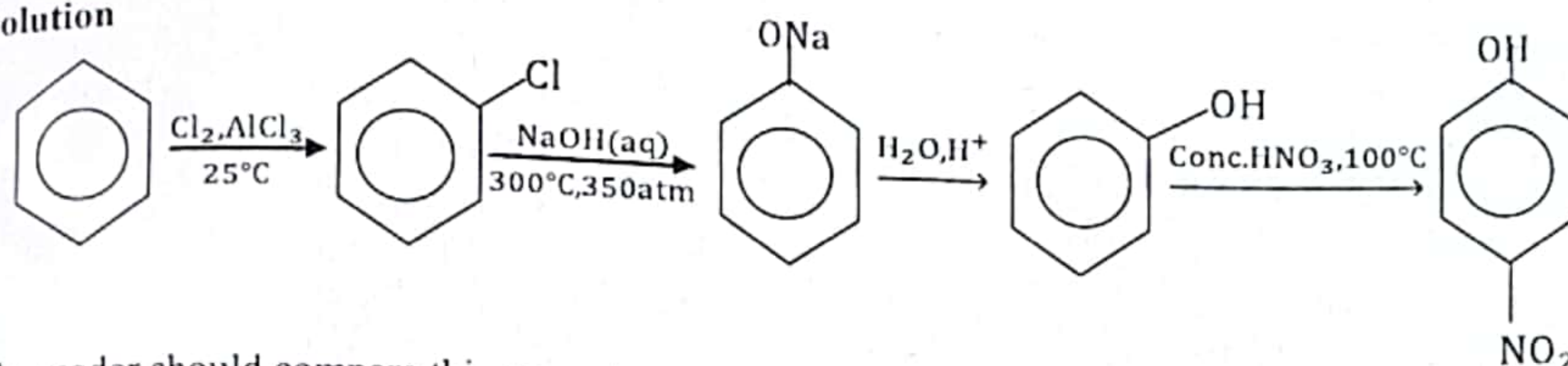
Solution



Example 33

Benzene into p-nitrophenol

Solution

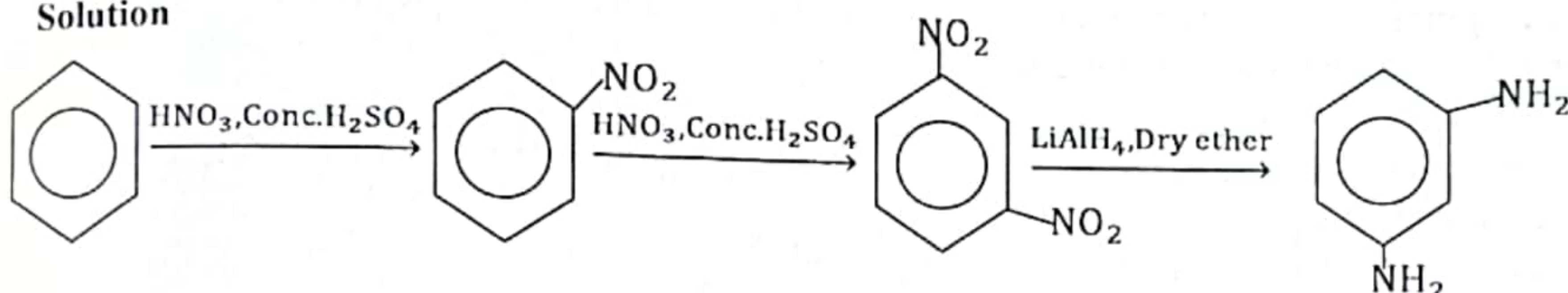


The reader should compare this example 33 with example 32 (here you should not leave Cl because ortho substituted product would be formed to greater extent. To make NO₂ to be at para position, Cl should be completely converted to OH before substituting NO₂).

Example 34

Convert benzene into m-aminoaniline

Solution



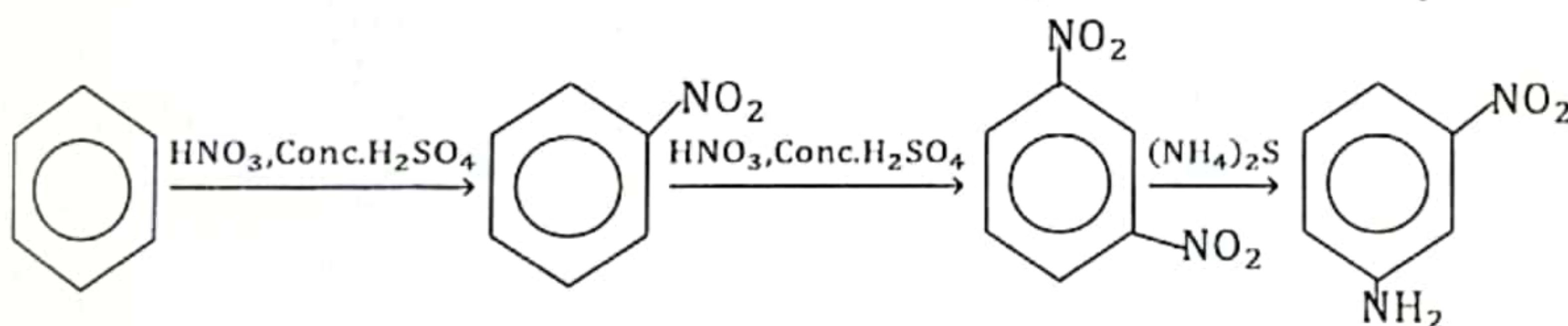
In the above example, LiAlH₄ in the third stage being strong reducing agent reduce all two NO₂ into NH₂; what about the following example?

Example 35

Convert benzene into m-nitroaniline

Solution

Here there is difficulty! Have you seen it? NO₂ and NH₂ are meta related so it suggest that NO₂ should be entered first, but how can we substitute NH₂? Let us see how the problem is solved!



The reader should recognise the importance of using (NH₄)₂S instead of other reducing agent like LiAlH₄ which reduces all NO₂ groups in the ring. But (NH₄)₂S is unable to reduce all NO₂ groups (it has ability of reducing only one NO₂ as shown in above example).

MISCELLANEOUS WORKED EXAMPLES ON CONVERSIONS

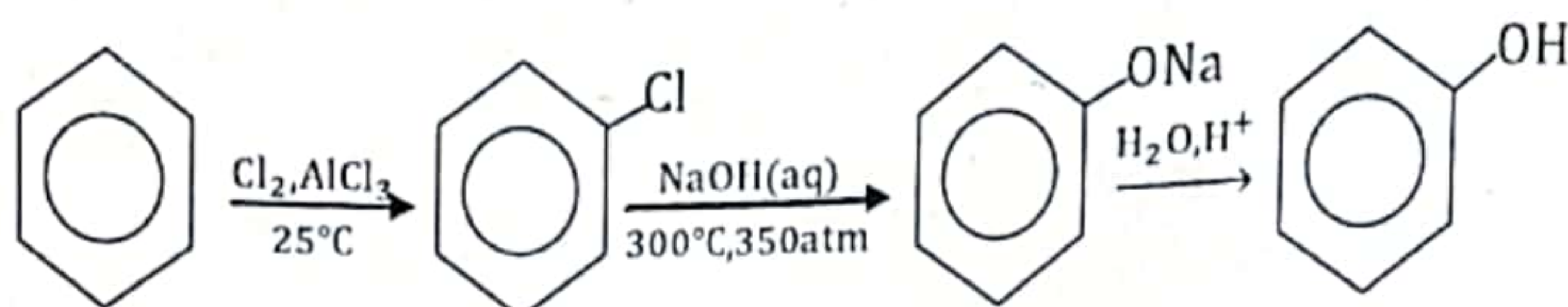
Example 36

Show how the following conversions may be achieved.

- Benzene into phenol
- 2-chloropropane into 1-iodopropane

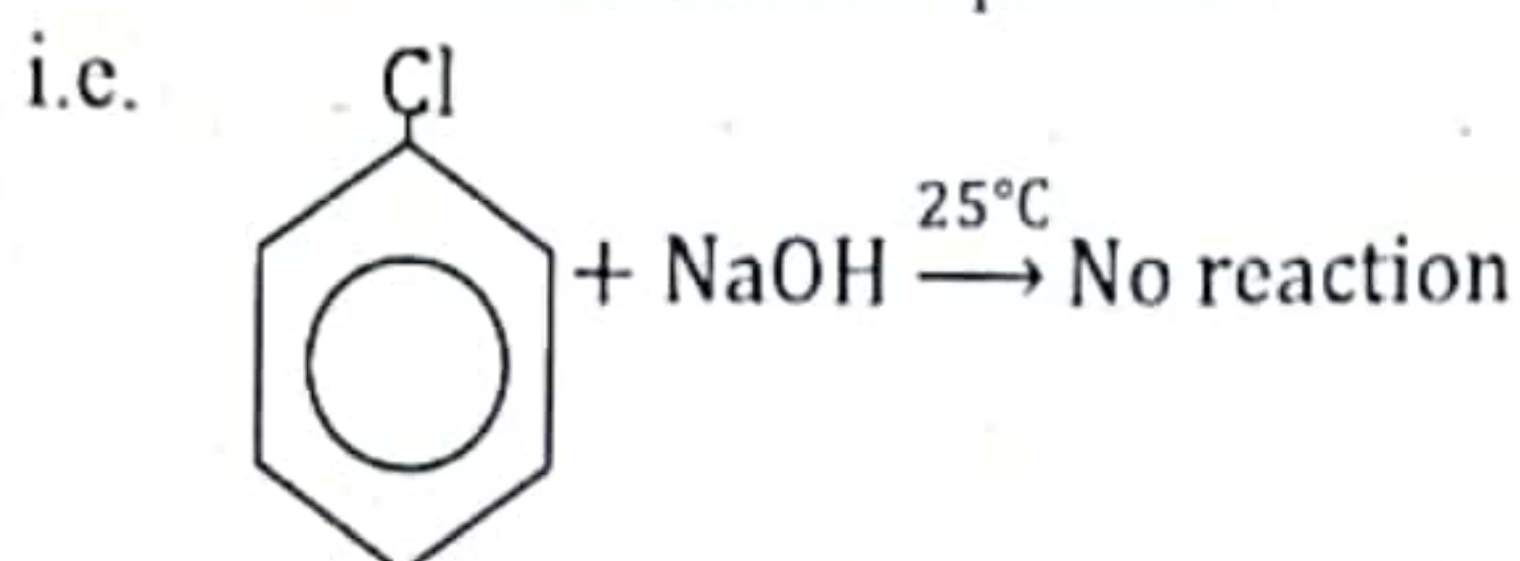
Solution

a)



Be careful!

- Many students do a mistake of converting chlorobenzene into phenol like in aliphatic haloalkane.
 $\text{R}-\text{Cl} + \text{NaOH} \xrightarrow{25^\circ\text{C}} \text{ROH} + \text{NaCl}$ Where R is alkyl group
- This must not be done in the case of chlorobenzene to phenol because existence of mesomerism in chlorobenzene leads to formation of $\text{C}=\text{Cl}$ thus making more difficult for chlorobenzene to undergo substitution reaction. Actually there is no chemical reaction between sodium hydroxide and chlorobenzene at room temperature.

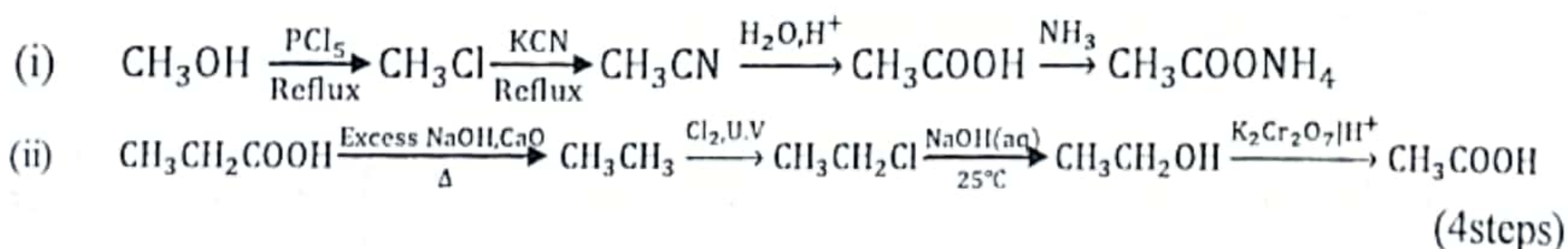


Example 37

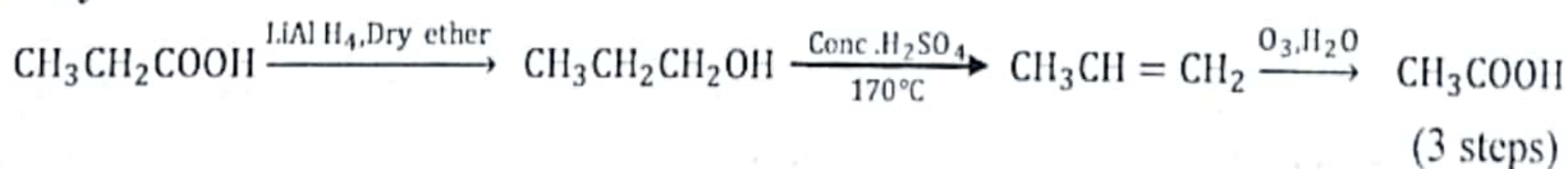
Show how you would carry the following conversions

- $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COONH}_4$
- $\text{CH}_3\text{CH}_2\text{COOH} \rightarrow \text{CH}_3\text{COOH}$

Solution



Alternatively

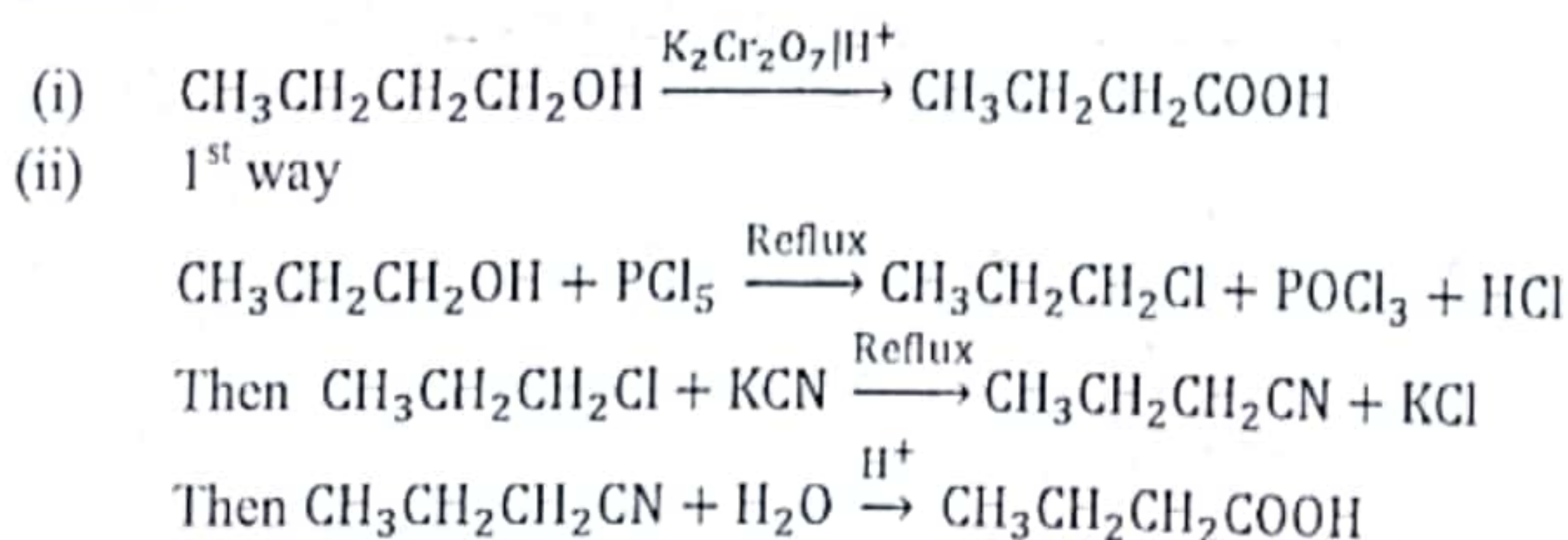


Example 38

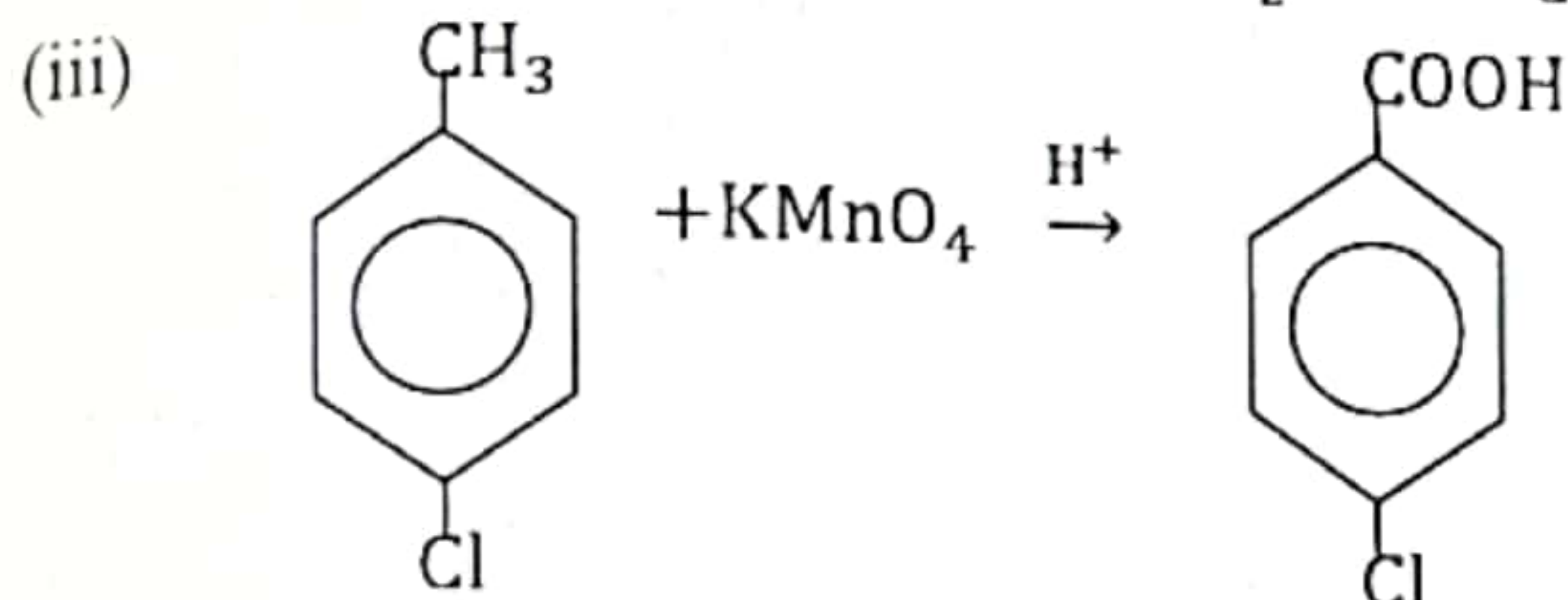
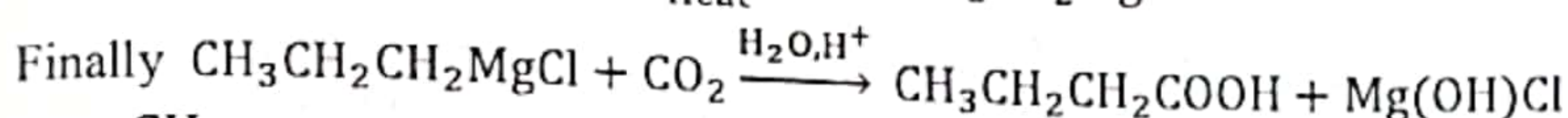
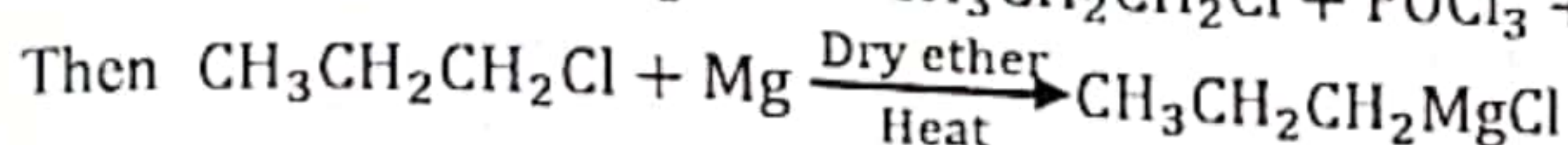
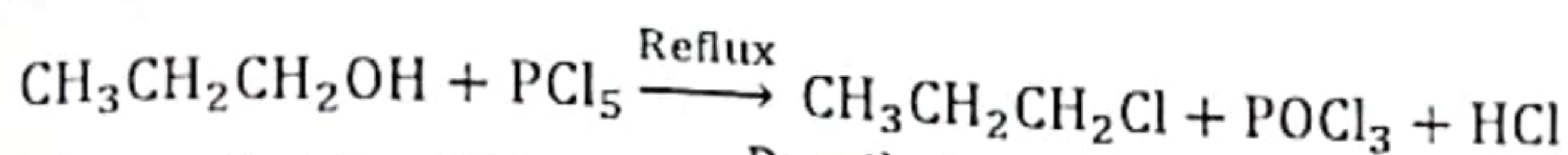
Give equations to illustrate good method to synthesize each of the following acids

- Butanoic acid from 1-butanol
- Butanoic acid from n-propyl alcohol. (2 ways)
- p-chlorobenzoic acid from p-chlorotoluene

Solution



2nd way



- $\text{K}_2\text{Cr}_2\text{O}_7$ may be used instead of KMnO_4

Example 39

With the help of chemical equations show clearly how the following conversion can be achieved.

- $\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{COOH}$
- $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH} \rightarrow \text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CHCH}_3}$

Solution

- $\text{CH}_3\text{CH}_2\text{Cl} + \text{NaOH(aq)} \xrightarrow{25^\circ\text{C}} \text{CH}_3\text{CH}_2\text{OH} + \text{NaCl}$
If dilute KOH is used instead of NaOH(aq), the temperature is 0°C
Then $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{CH}_3\text{COOH}$
- $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH} + \text{H}_2 \xrightarrow{\text{Pd/BaSO}_4} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$
Then $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CHCH}_3}$

Example 40

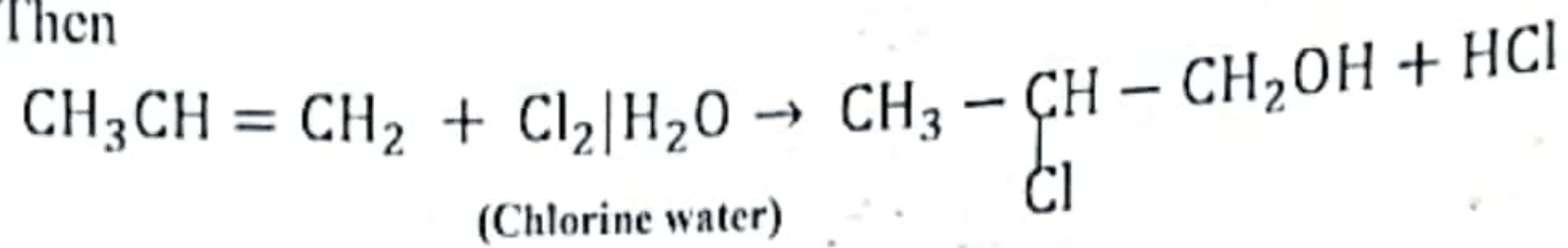
Write down the equation showing how each of the following conversions could be affected (more than one reaction will be required in each case)

- 1 - bromobutane into 2 - bromobutane
- 2 - bromobutane into 2 - bromopropane
- 1 - chloropropane into 2 - chloropropanol

Solution

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{conc. KOH} \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
Then $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CHCH}_3}$
- $\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CHCH}_3} + \text{conc. KOH} \xrightarrow[\Delta]{\text{CH}_3\text{CH}_2\text{OH}} \text{CH}_3\text{CH} = \text{CHCH}_3 + \text{KBr} + \text{H}_2\text{O}$
Then $\text{CH}_3\text{CO} - \text{H} + \text{CH}_3\text{MgI} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{CH}_3\underset{\text{OH}}{\text{CHCH}_3} + \text{Mg(OH)I}$
Finally $\text{CH}_3\underset{\text{OH}}{\text{CHCH}_3} + \text{PBr}_3 \rightarrow \text{CH}_3\underset{\text{Br}}{\text{CHCH}_3} + \text{H}_3\text{PO}_3$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{conc. KOH} \xrightarrow[\Delta]{\text{CH}_3\text{CH}_2\text{OH}} \text{CH}_3\text{CH} = \text{CH}_2 + \text{KCl} + \text{H}_2\text{O}$

Then

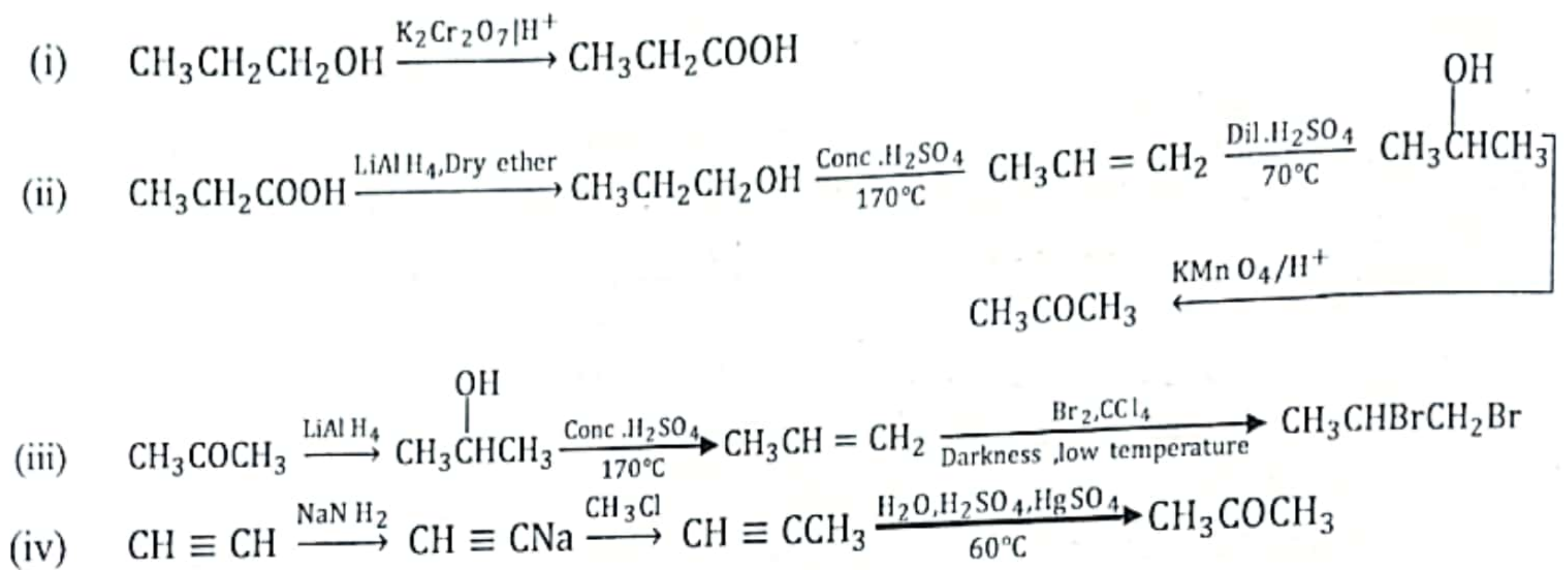


Example 41

Show how the following conversions may be achieved. Experimental details of conversions are not required

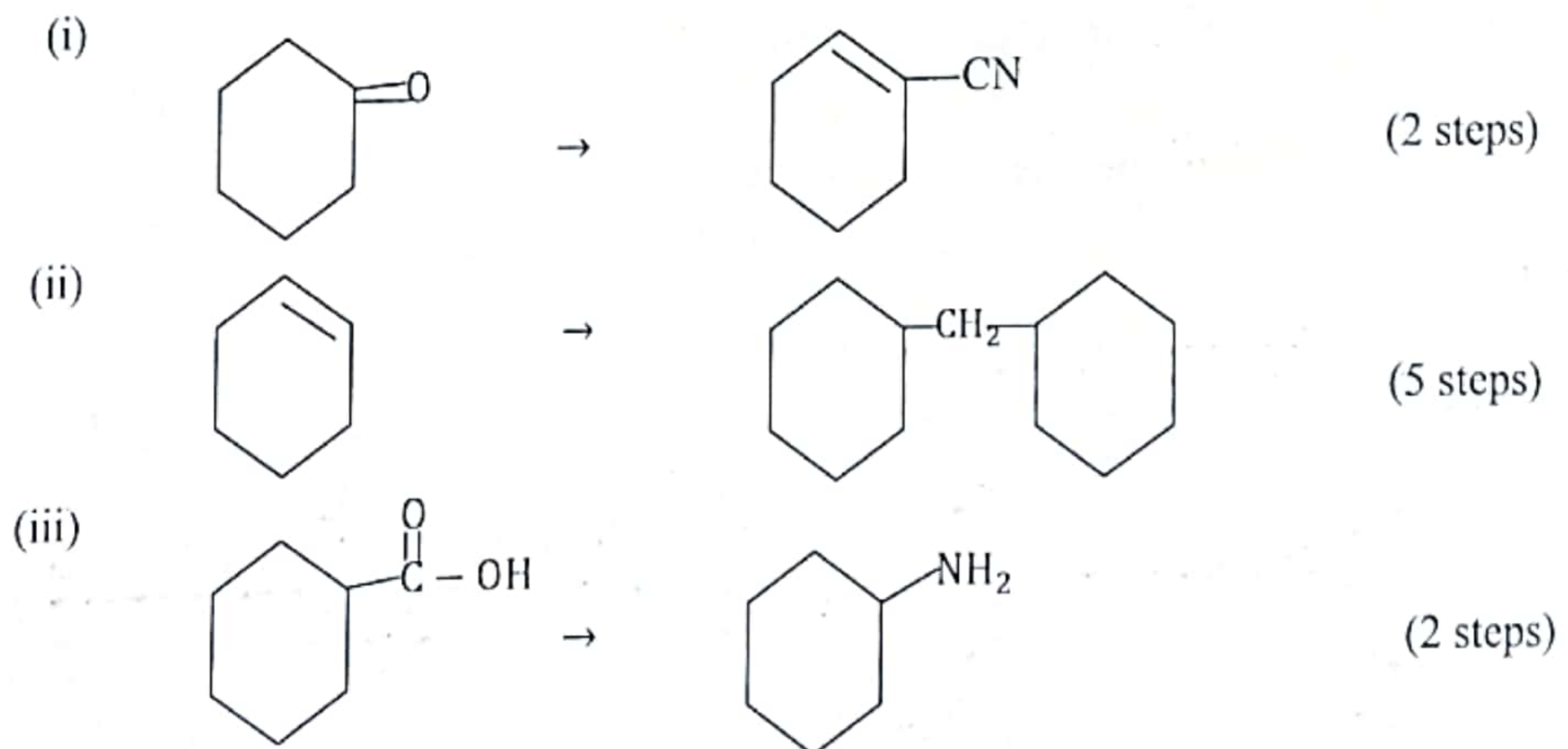
- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ to $\text{CH}_3\text{CH}_2\text{COOH}$
- (ii) $\text{CH}_3\text{CH}_2\text{COOH}$ to CH_3COCH_3
- (iii) CH_3COCH_3 to $\text{CH}_3\text{CHBrCH}_2\text{Br}$
- (iv) $\text{CH}\equiv\text{CH}$ to CH_3COCH_3

Solution

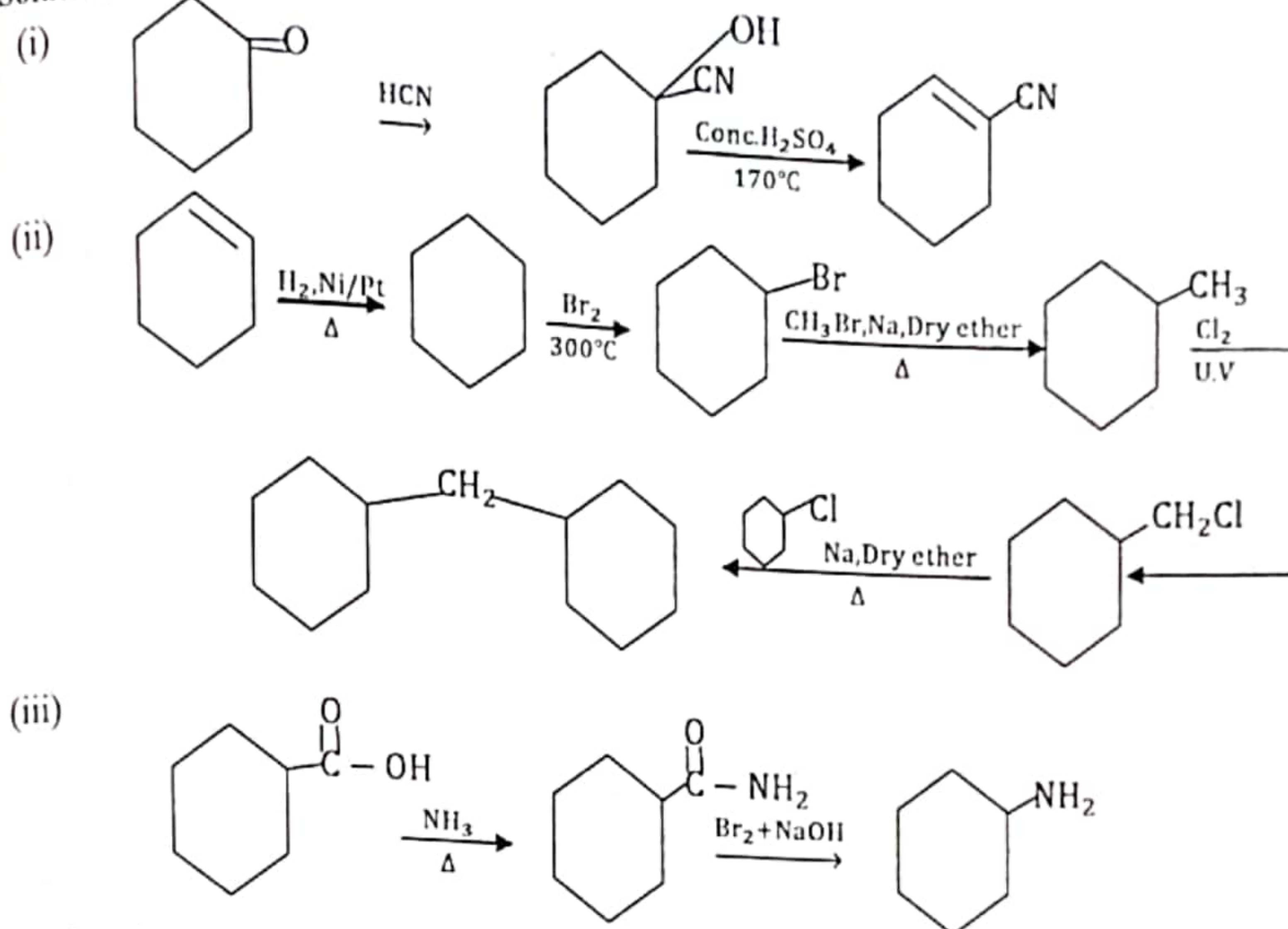


Example 42

Show how the following conversions can be carried out under given restrictions;



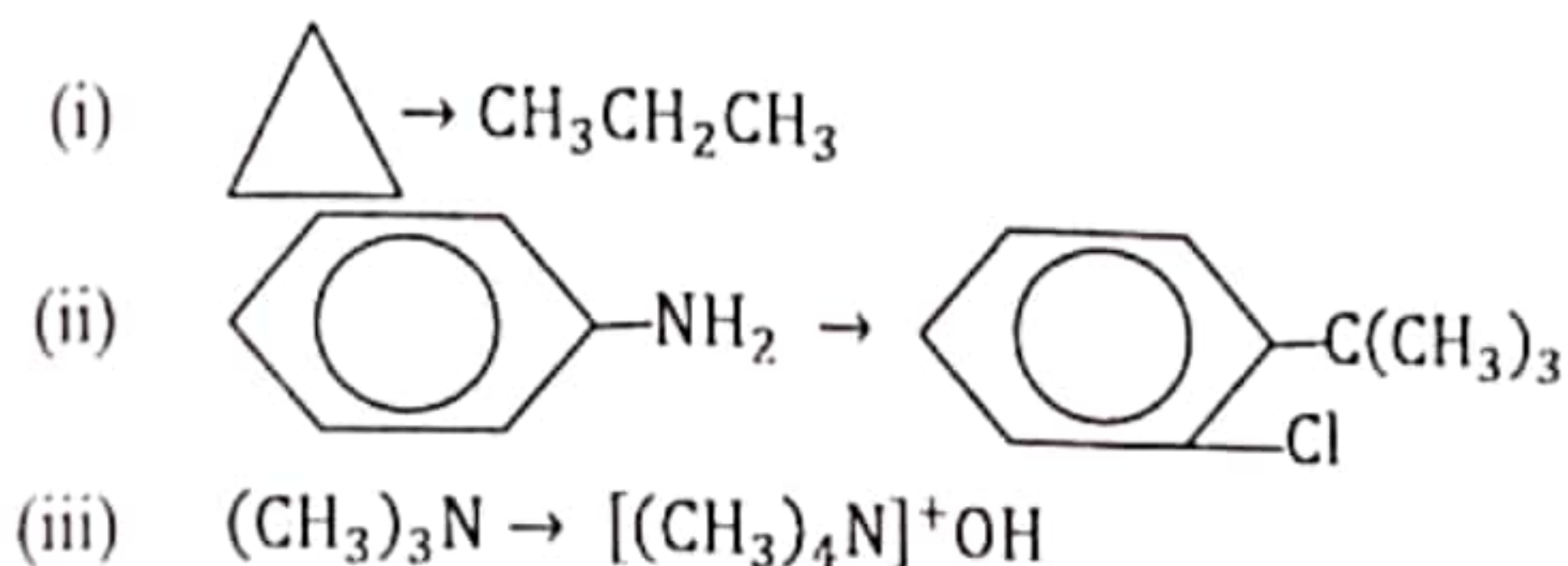
Solution



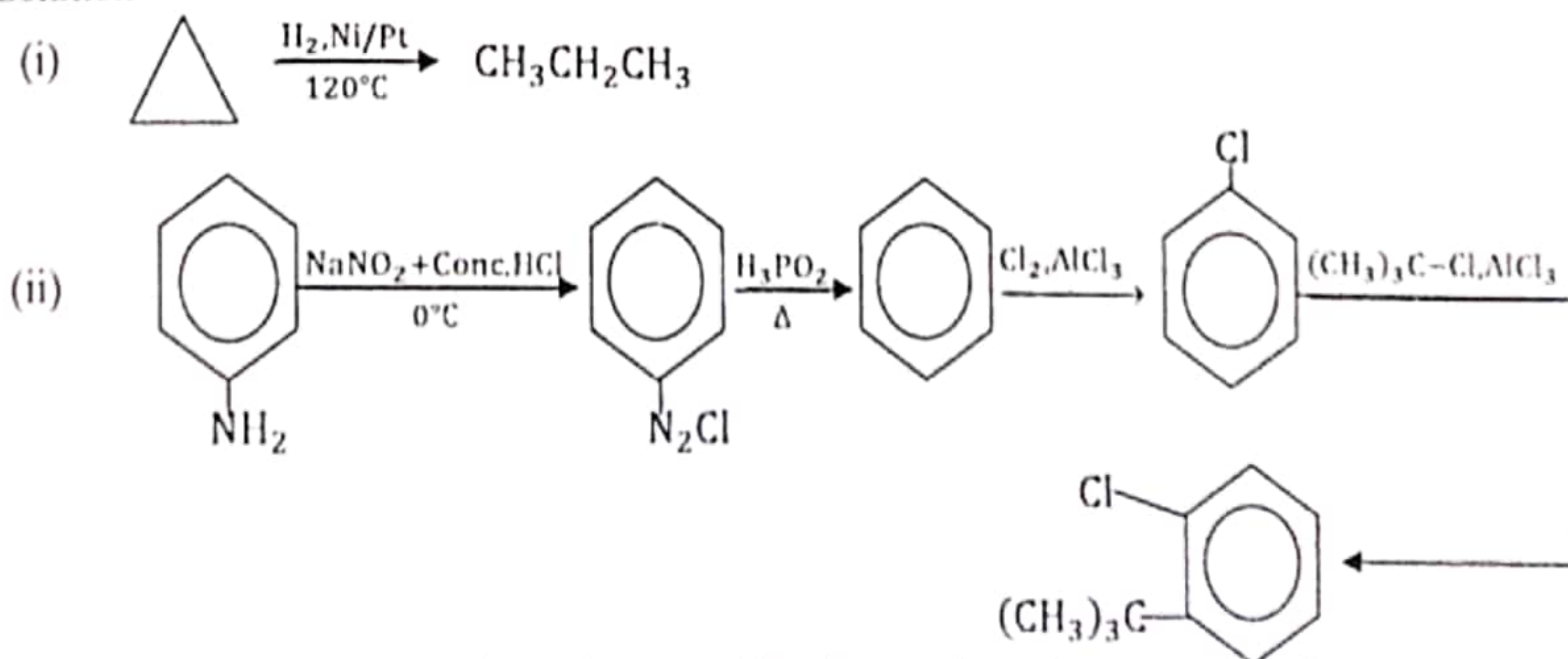
- $(\text{NH}_4)_2\text{CO}_3$ can be used instead of NH_3

Example 43

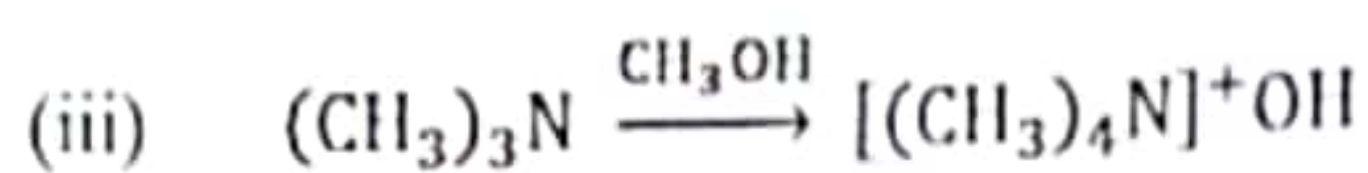
Show how the following conversions can be affected:



Solution

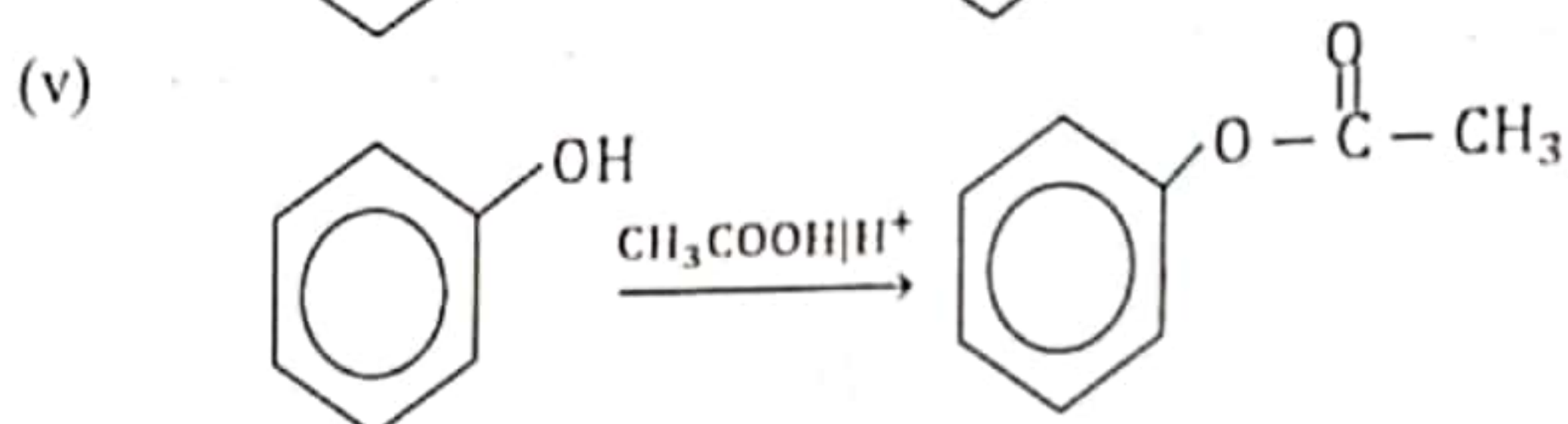
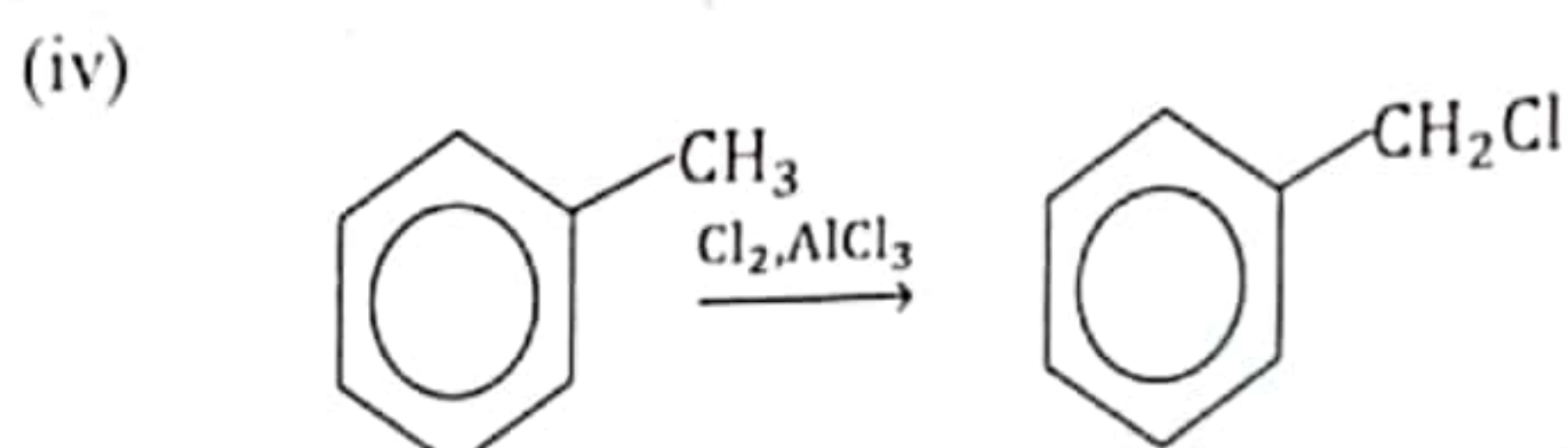
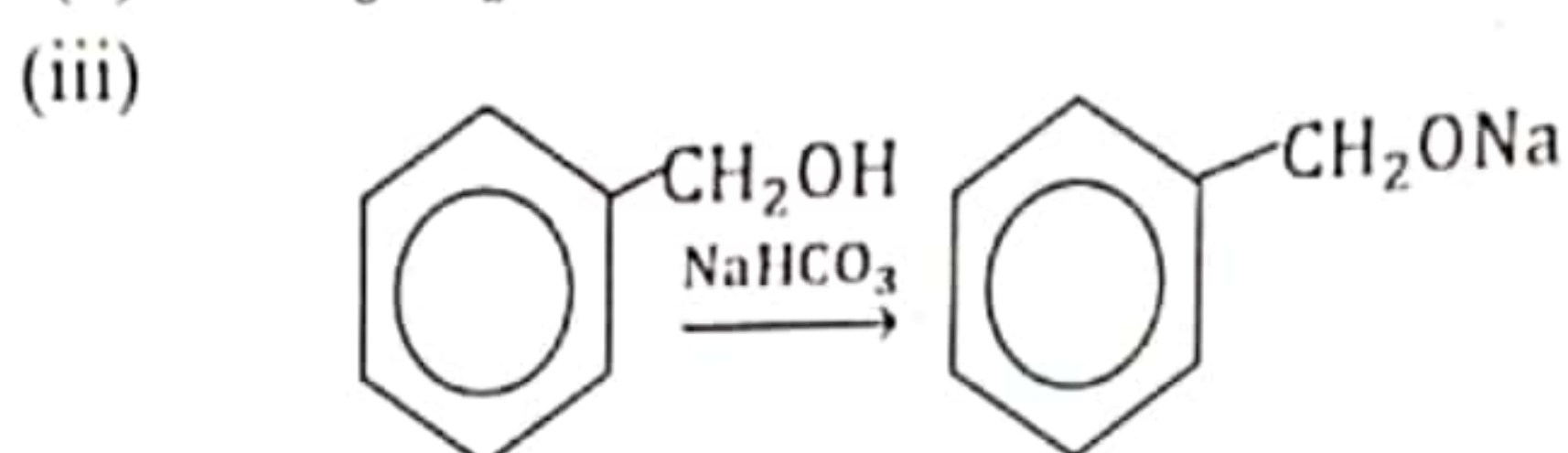
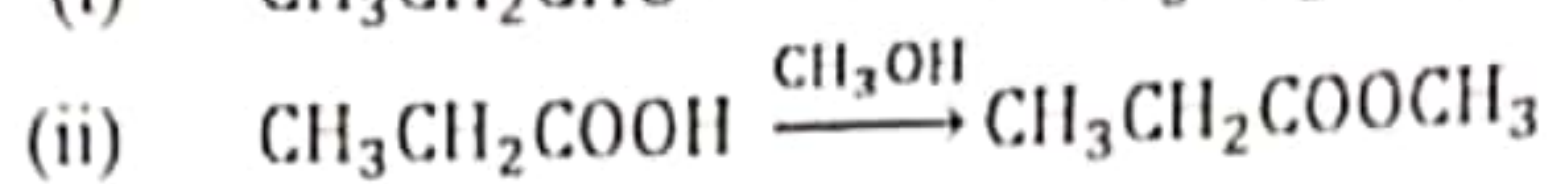
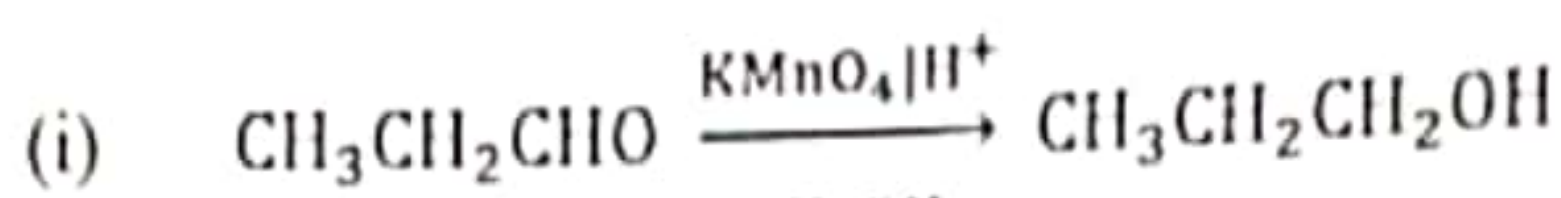


- It should be noted that; Cl must be entered first because it has lower steric hindrance to enable formation of the ortho product.



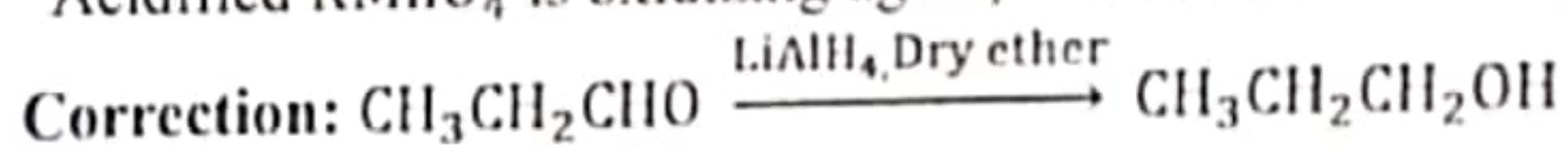
Example 44

In an examination paper, a student offered conditions or chemicals necessary for the conversions of organic compound to take place as shown below. Study them carefully and for these conversions which were provided with wrong conditions of chemicals, rewrite them and show the correct conditions or chemicals which must be presented for the conversions to be carried out.



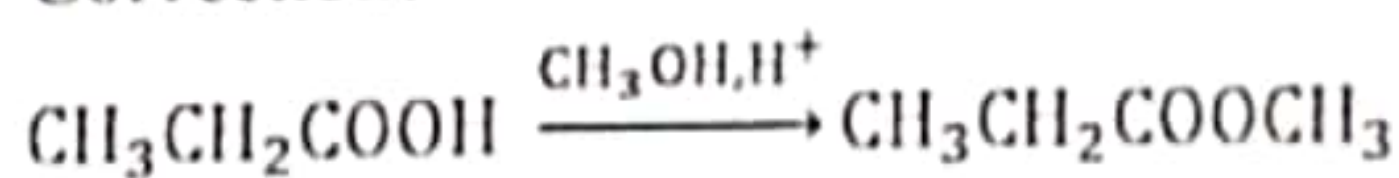
Solution

- (i) Acidified KMnO_4 is oxidizing agent, it would oxidize the given aldehyde to carboxylic acid.



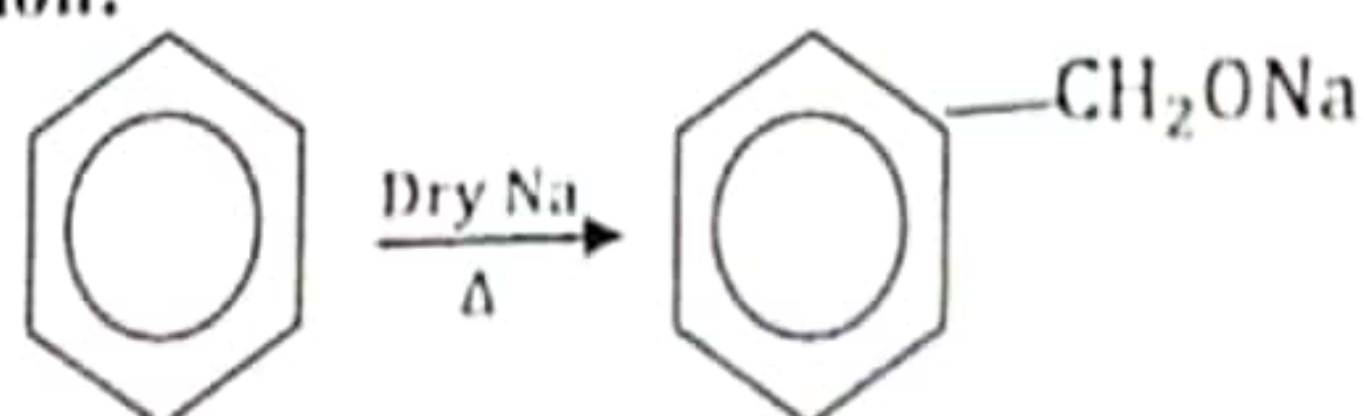
- (ii) carboxylic acid cannot react with alcohol (Esterification) in absence of acidic medium (sulphuric acid)

Correction:



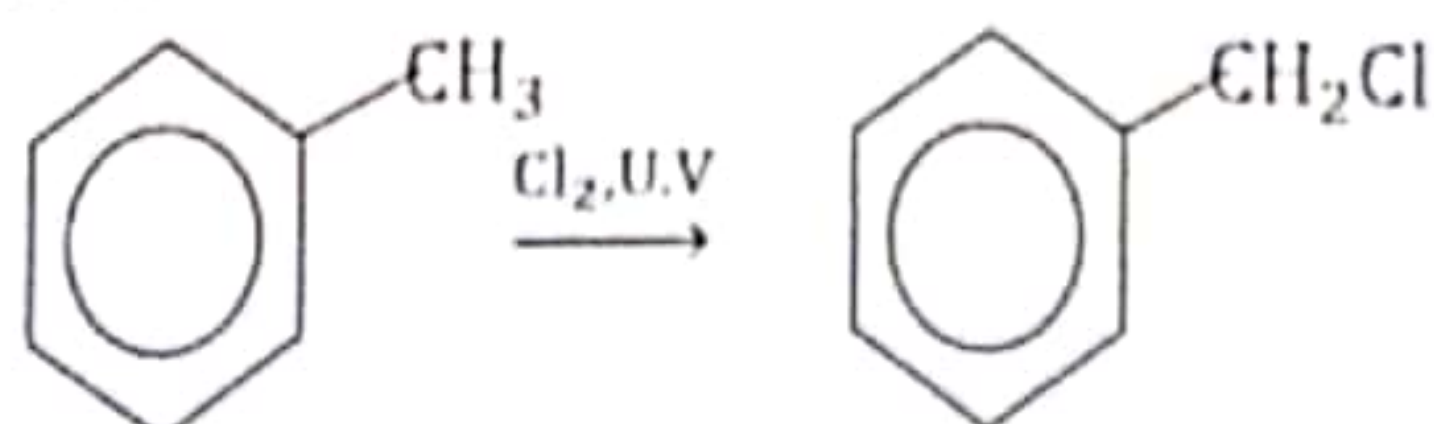
- (iii) Sodium bicarbonate (NaHCO_3) cannot react with alcohol because both have similar basic characters

Correction:

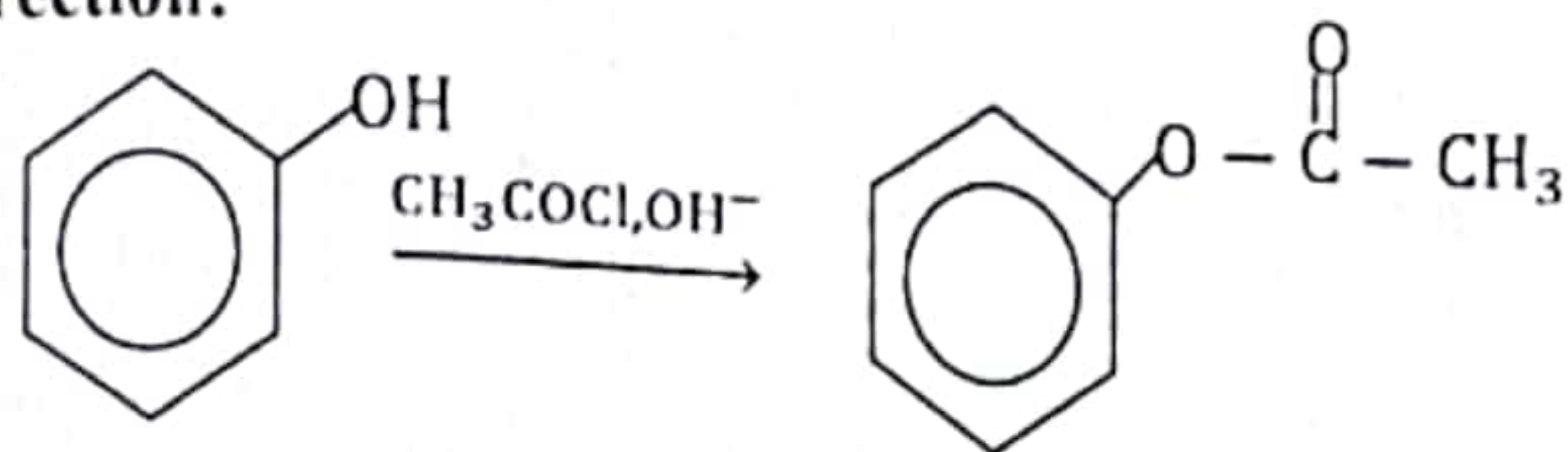


- (iv) Presence of AlCl_3 (Lewis acid) favours occurrence of electrophilic substitution reaction in benzene ring (and not free radical substitution reaction in the side chain)

Correction:



- (v) Phenol cannot react with carboxylic acid because both have similar acid characters
Correction:

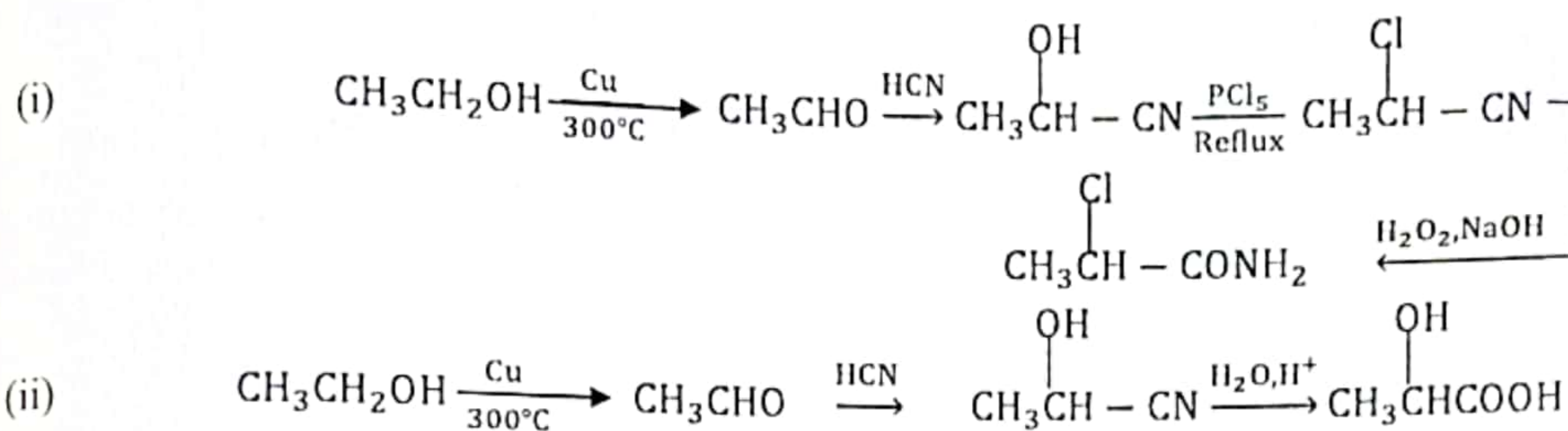


Example 45

How would you convert?

- (i) Ethanol into 2-chloropropanamide
 (ii) Ethanol into 2-hydroxypropanoic acid

Solution



PRACTICE EXERCISE 25

Problem

Show how you would achieve the following conversions: (laboratory details are not required).

- i. Methane into propanoic acid (not more than 3 steps)
- ii. Benzene into ethanoic acid (not more than 3 steps)
- iii. Ethanol into propanone.
- iv. Starch into ethanoic acid
- v. $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$ into $\text{CH}_2 = \text{CH}_2 - \text{COOH}$
- vi. Carbon dioxide into benzene.
- vii. Limestone into ethyne
- viii. $\text{CH}_3\text{CH}_2\text{OH}$ into $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{COOH}$
- ix. Aspirin into benzene
- x. Vanillin into anisole

Chapter 26

CHEMICAL TESTS AND DISTINCTIONS OF ORGANIC COMPOUNDS

Generally a **chemical test** is a quantitative or qualitative procedure designed to prove the existence or quantity of a chemical compound with the aid of specific reagent.

- In organic chemistry, chemical tests are very useful in identification of various organic compounds by testing functional groups present in the compounds.

One important feature for a chemical reaction to act as a chemical test in normal laboratory is that: **it must give a change which we can observe physically.**

- In other words, it must give a change we can see by eyes, smell by nose, hear by ears or something we can taste (for products which are not serious poisonous).
- So one key point, the student should understand here is that: **on explaining chemical test, the explanation must base on the physical observations.**

Warning!

Most students make a mistake on explaining the chemical tests by just saying "with certain reagent, one compound will react and another compound will not react" how will you recognise here there is a chemical reaction and there, there is no reaction? The answer of this question is based on physical observation and is what explanation of chemical test is all about! It is simply like, like 'here' colour 1 is observed, while 'there' colour 2 is observed.

- In this chapter, various chemical tests discussed in previous chapters and some new tests are assembled together and are discussed more systematically, in such a way that they can be memorised easily.

Liquid bromine test

Liquid bromine is the normal molecular bromine which is diatomic.

- Its formula is Br_2
- Its colour is reddish-brown

The liquid is very useful test of different organic compounds listed below

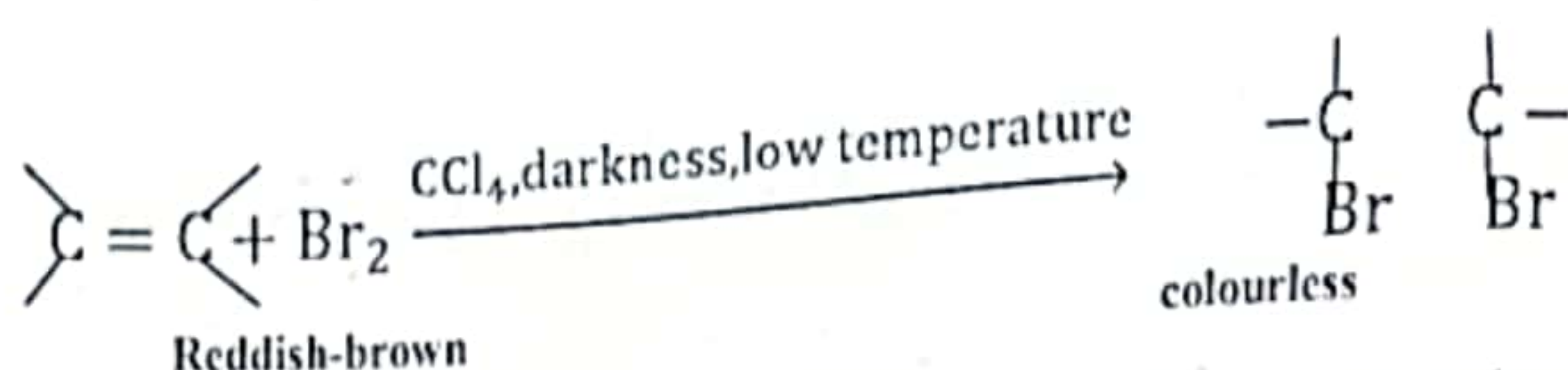
(i) Unsaturated aliphatic organic compounds

Unsaturated aliphatic organic compounds give positive liquid bromine test by decolourising reddish-brown colouration of the bromine. These unsaturated aliphatic organic compounds may contain $\text{C} = \text{C}$ or $\text{C} \equiv \text{C}$

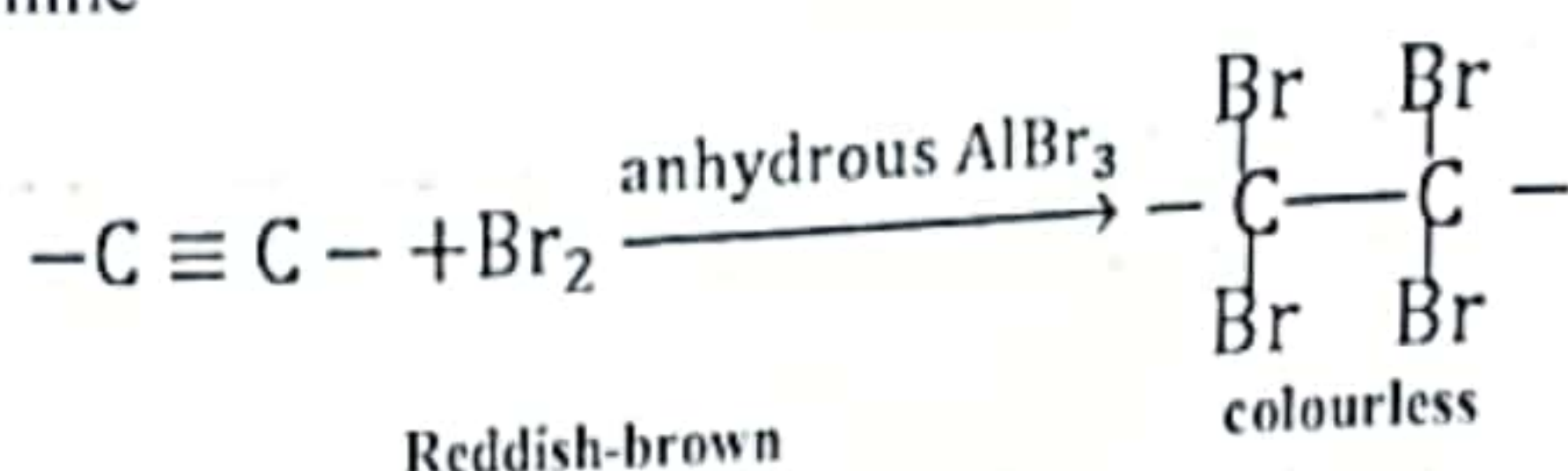
- For compounds with $\text{C} = \text{C}$, associated conditions for the reactions to take place, are presence of:
 - Darkness
 - Low temperature
 - Tetrachloromethane (common name is carbon tetrachloride), CCl_4 .

Therefore in one sentence!

"Under darkness and low temperature, compounds with $\text{C} = \text{C}$, decolourise reddish-brown colouration of liquid bromine in presence of CCl_4 ."



- For compounds with $\text{C} \equiv \text{C}$, associated conditions for the reaction to take place is the presence of **Lewis acid catalyst**, mainly AlBr_3 .
- Therefore, “in presence of anhydrous AlBr_3 , compounds with $\text{C} \equiv \text{C}$, decolourise reddish-brown colouration of liquid bromine”



So the liquid bromine test is very useful in distinction of unsaturated aliphatic organic compounds from saturated organic compounds.

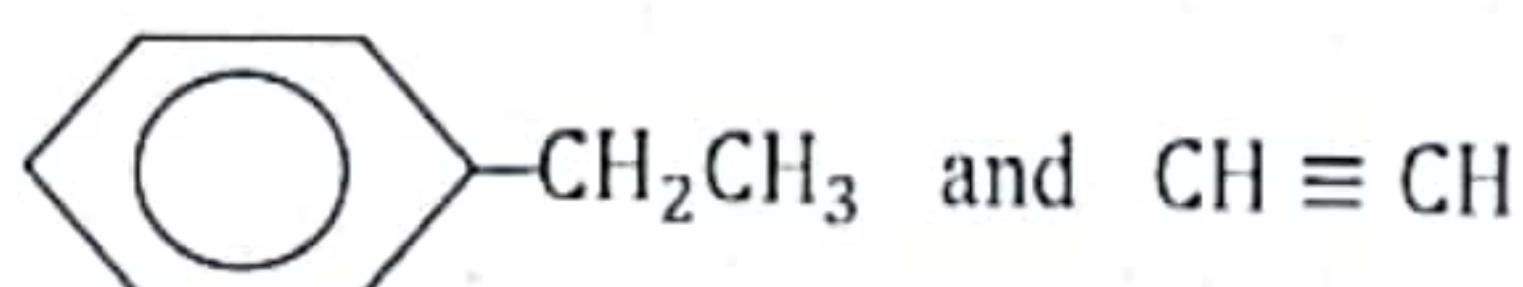
Question

With the help of chemical equations, give a chemical test to distinguish between the following pairs of organic compounds:

- Propene and propane
- $\text{CH}_2 = \text{CH} - \text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- $\text{CH} \equiv \text{CH}$ and CH_3CH_3
- $\text{CH} \equiv \text{CH} - \text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{NH}_2$

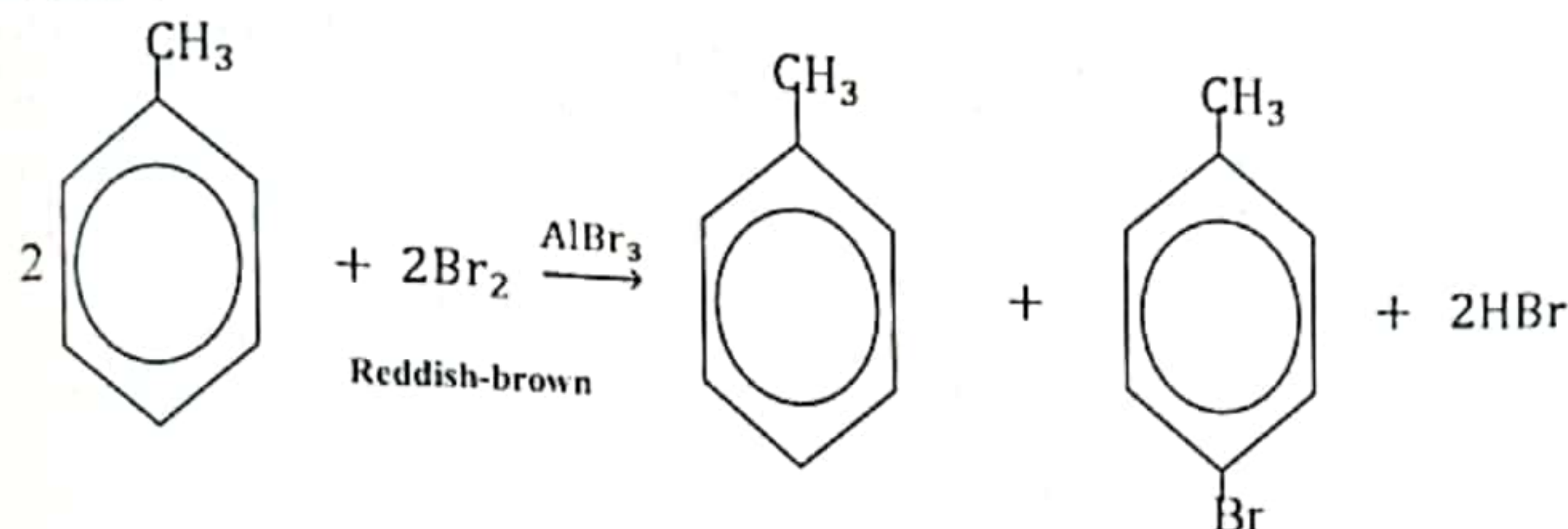
Warning!

- In distinguishing unsaturated hydrocarbon from alkane by using this method, don't just say that, “unsaturated hydrocarbons (alkene and alkyne) decolourises reddish-brown colouration of the liquid bromine while alkane does not”. This is because even alkanes can decolourise the liquid bromine, but in presence of ultraviolet light or very high temperature. So you must mention conditions for the reaction to avoid this confusion. For example in (i) above the explanation would look like, “under darkness and low temperature, propene decolourises reddish-brown colouration of bromine while propane does not”.
- Don't use liquid bromine test to distinguish alkyne from compound with alkyl group attached to benzene ring. For example:



- This is because, bromination of alkyne requires Lewis acid catalyst (AlBr_3), the catalyst which also activate electrophilic substitution reaction in the benzene and hence both of the two compounds will decolourise the liquid bromine.
- (ii) **Compounds with benzene ring**
Under presence of Lewis acid catalyst (like AlBr_3 and FeBr_3) compounds with benzene ring decolourise reddish-brown colouration of benzene.

– For example:



So the liquid bromine test is very useful in distinguishing compounds which contains benzene ring from those which do not contain benzene ring.

Question

Describe chemical test to distinguish the following pairs of organic compounds

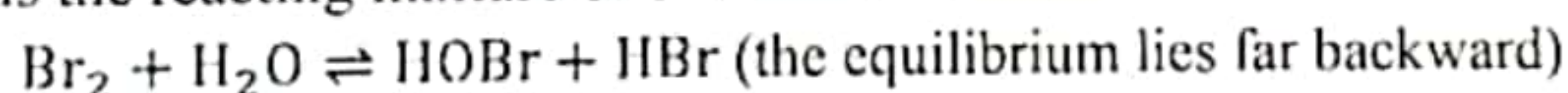
- (i) and CH_3CH_3
- (ii) and $\text{CH}_3\text{CH}_2\text{OH}$
- (iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ and
- (iv) and $\text{CH}_2=\text{CH}_2$

- (v) Benzene and hexane

(Don't forget to consider directing effect of substituent in the benzene if you are asked to include the chemical equation)

Bromine water test

Bromine water is the reacting mixture of bromine and water.

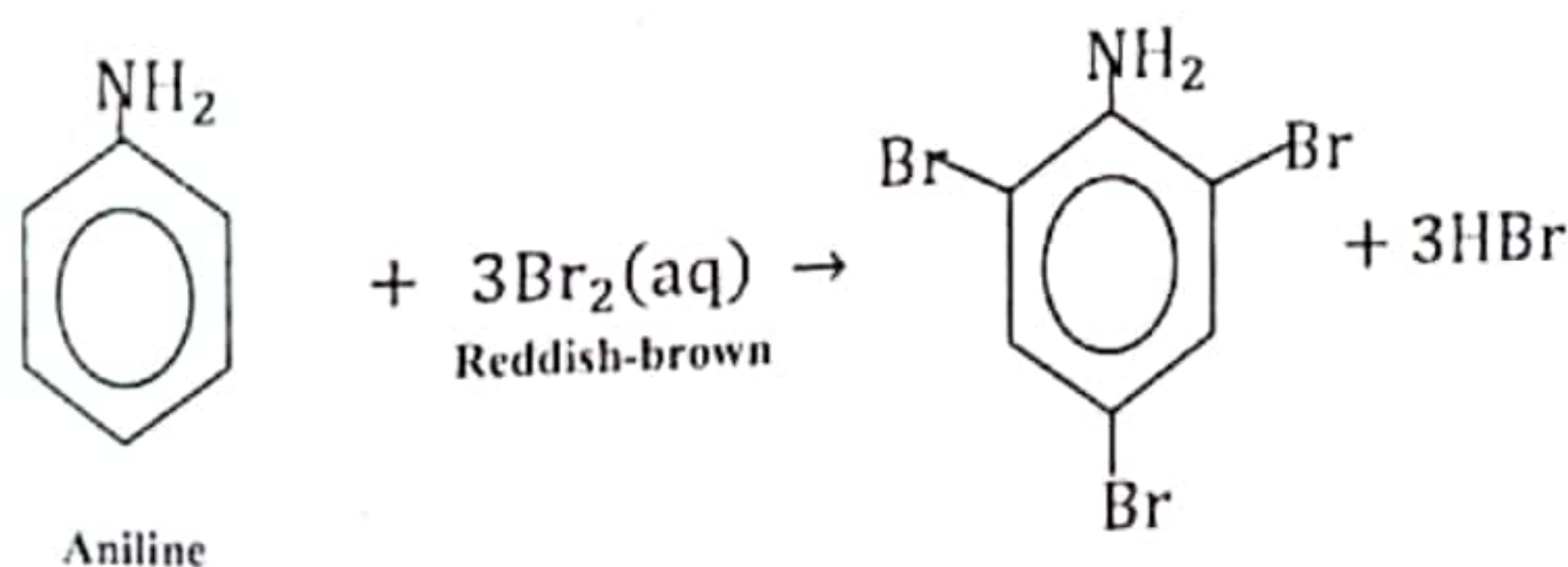


- It always written as $\text{Br}_2 \mid \text{H}_2\text{O}$ where the vertical line indicates that the two components are in contact (or mixed) to each other.
- Its colour is reddish-brown.

The bromine water test is very useful test of different organic compounds listed below.

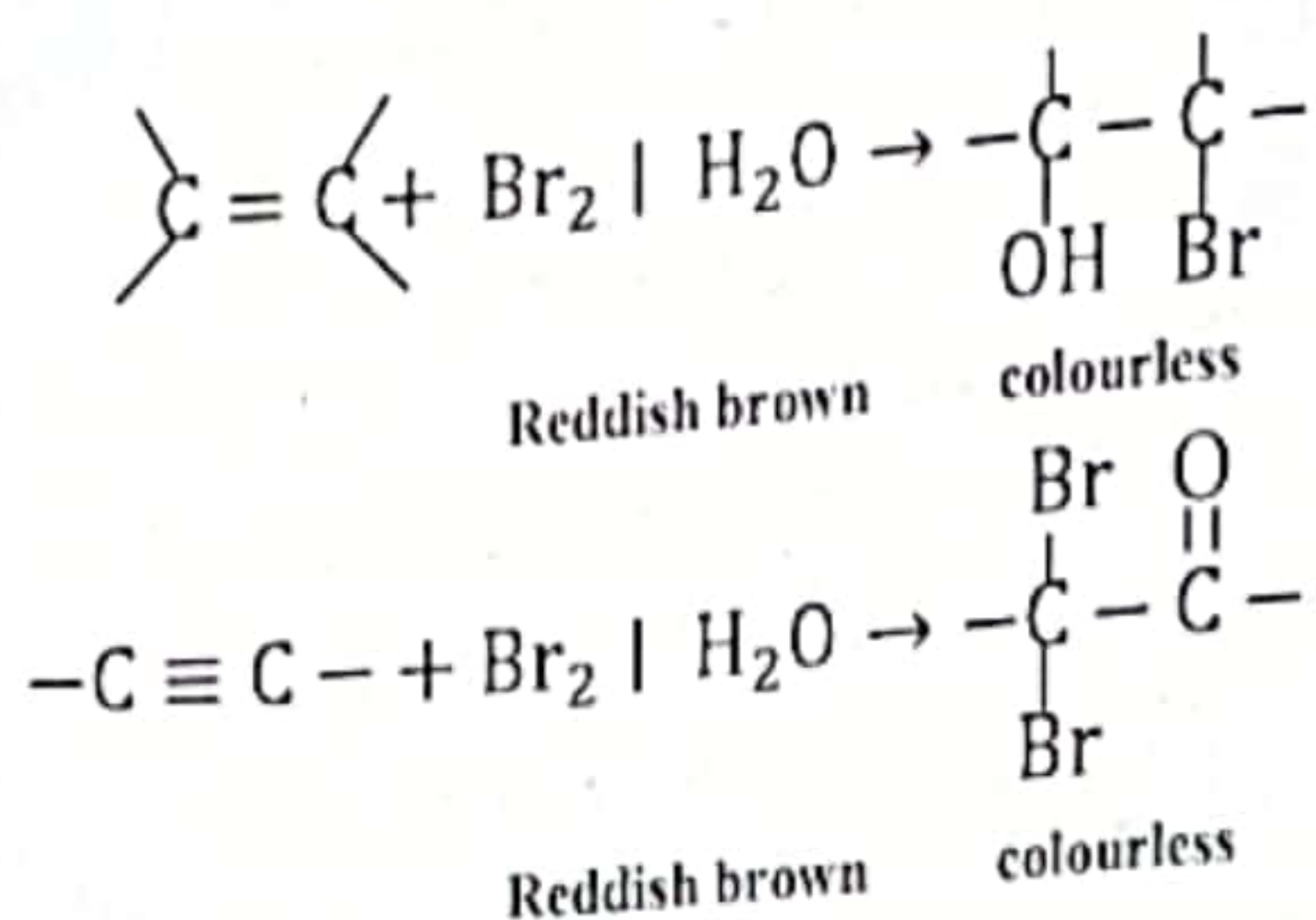
(iii) Aniline

Like phenol, this also gives positive bromine water test by giving 2,4,6-tribromoaniline and reddish-brown colouration of bromine water disappear



(i) Unsaturated aliphatic organic compounds

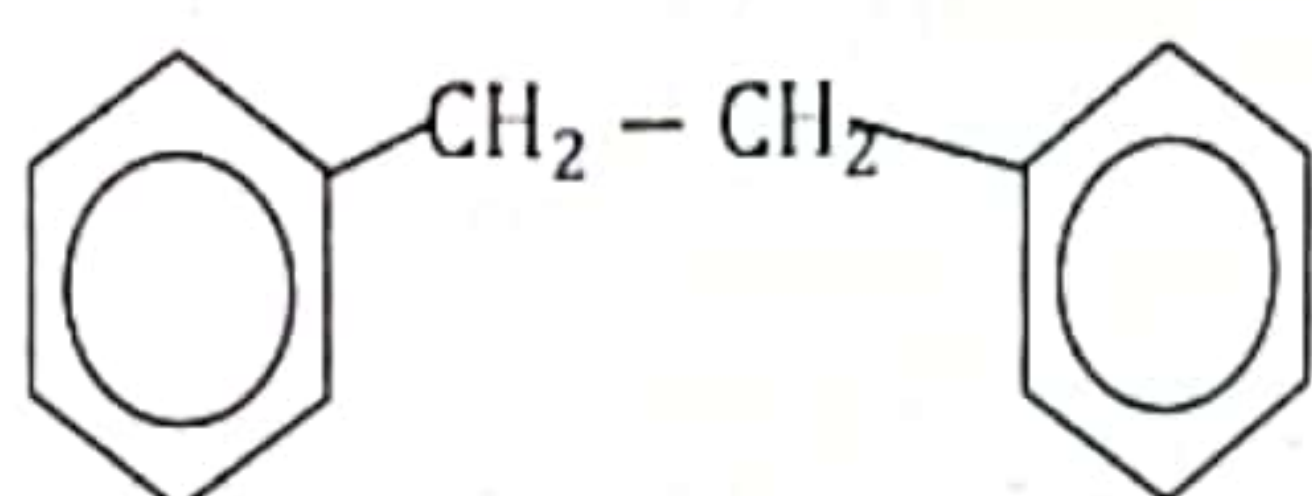
These give positive bromine water test by decolourising reddish-brown colouration of the bromine.



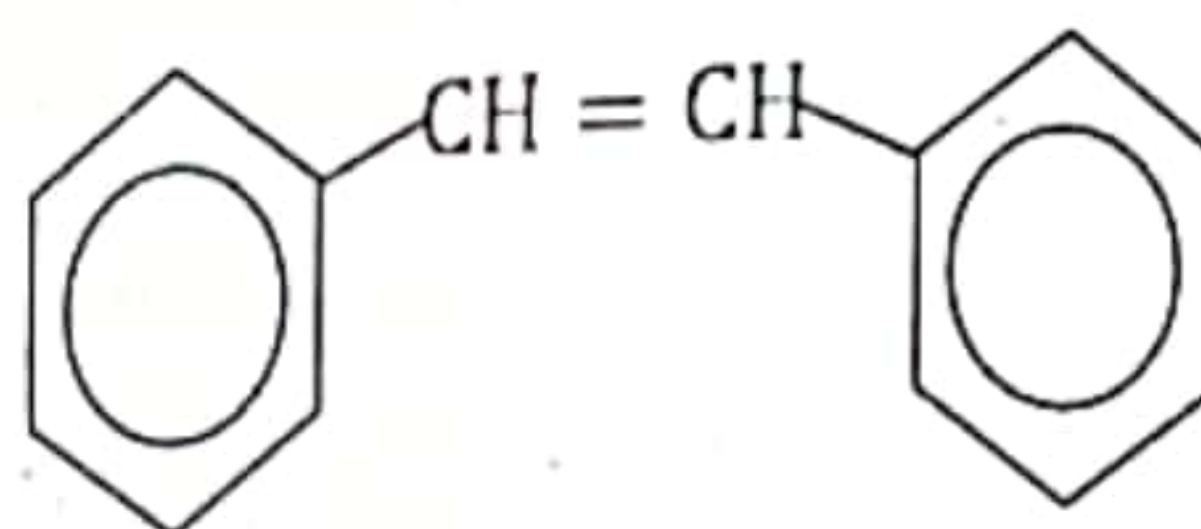
Question

Explain chemical test to distinguish the following pair of organic compounds

i.



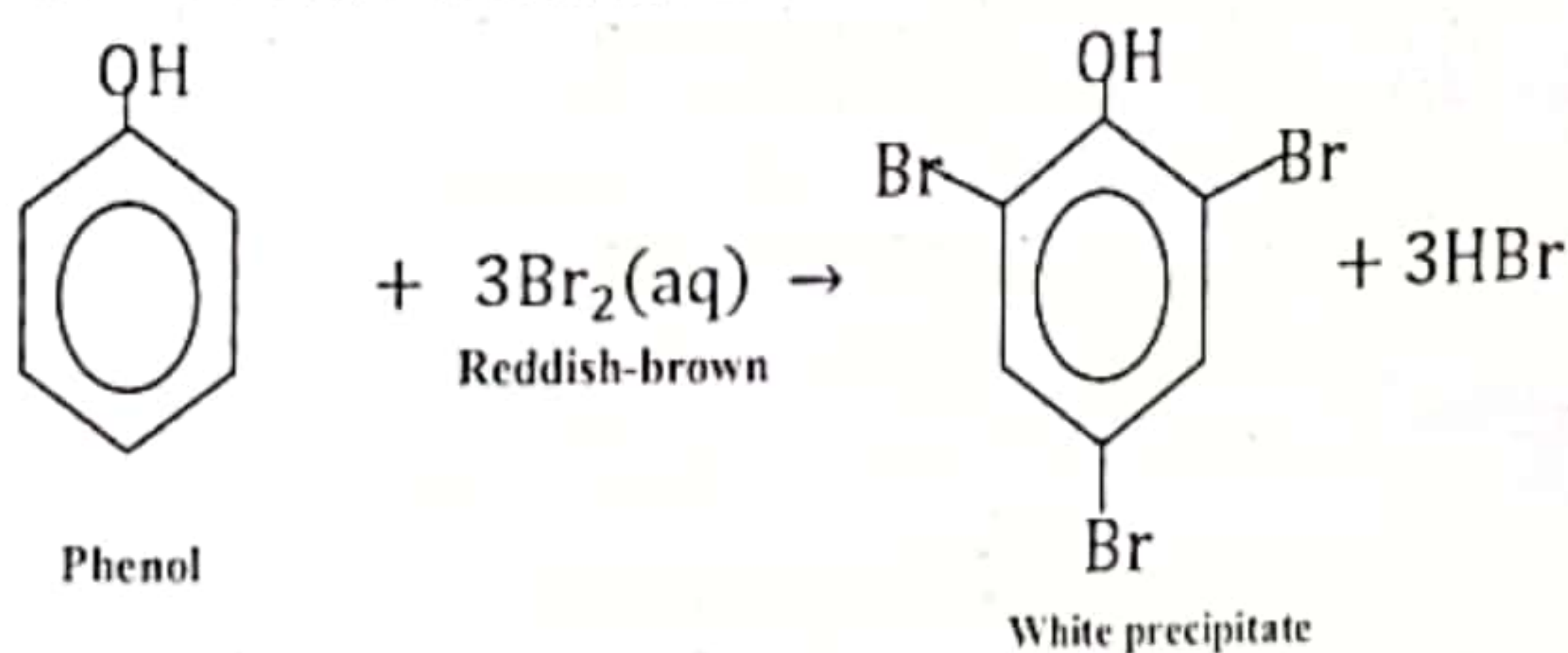
And



ii. Cumene and styrene

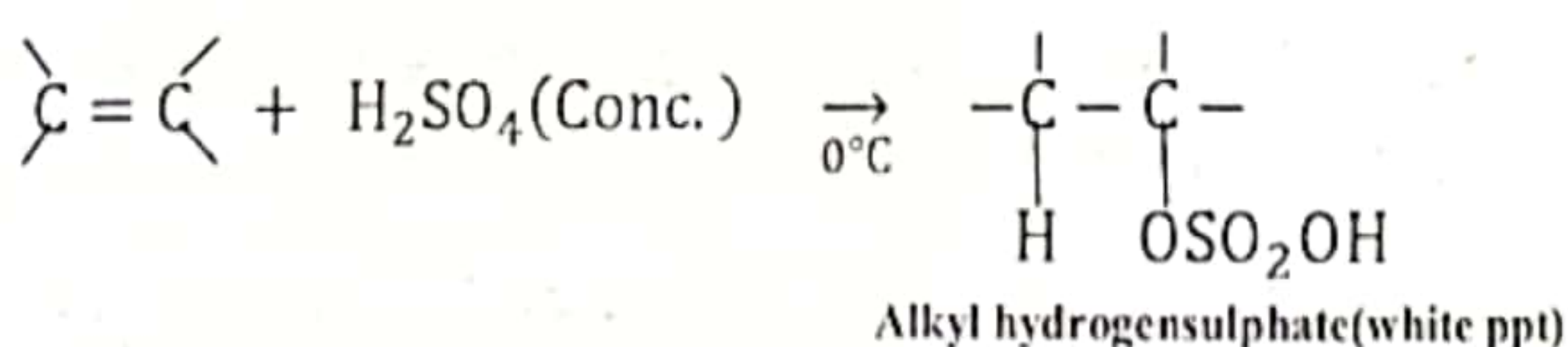
(ii) Phenol

This give bromine water test by giving white precipitate of 2, 4, 6-tribromophenol and reddish-brown colouration of bromine water disappear.



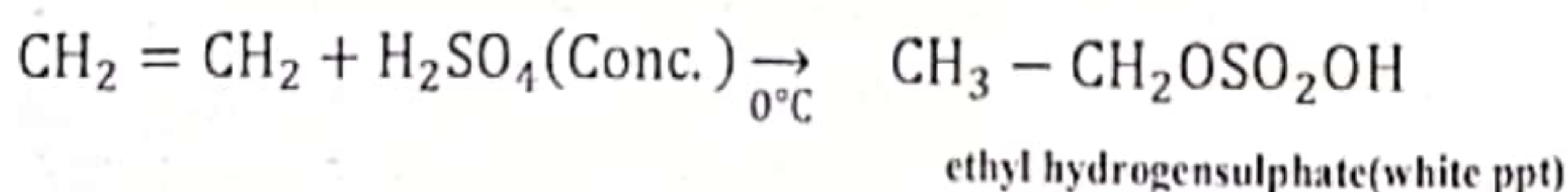
Cold concentrated sulphuric acid test

Cold sulphuric acid test is very useful test of compound with $\text{C}=\text{C}$ by giving white precipitate of hydrogensulphate.

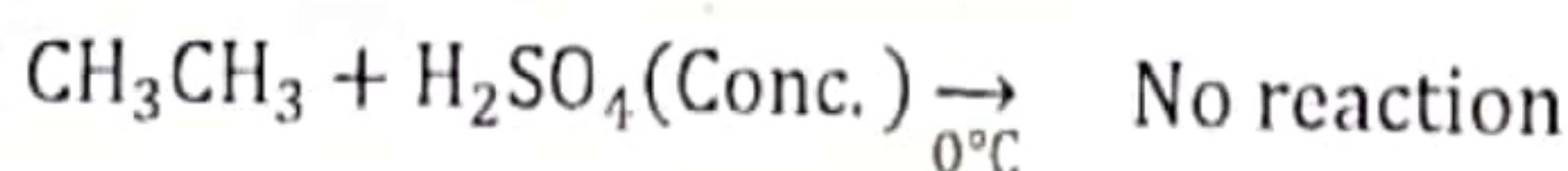


– So the test is very useful in distinguish alkenes from alkane.

For example:



While



In words: with cold concentrated sulphuric acid, ethene gives white precipitate while ethane does not.

Potassium permanganate test

Potassium permanganate is very strong oxidising agent.

- Its formula is KMnO_4 (It actually complex compound with the formula $\text{K}[\text{MnO}_4]$)
- Its colour is purple

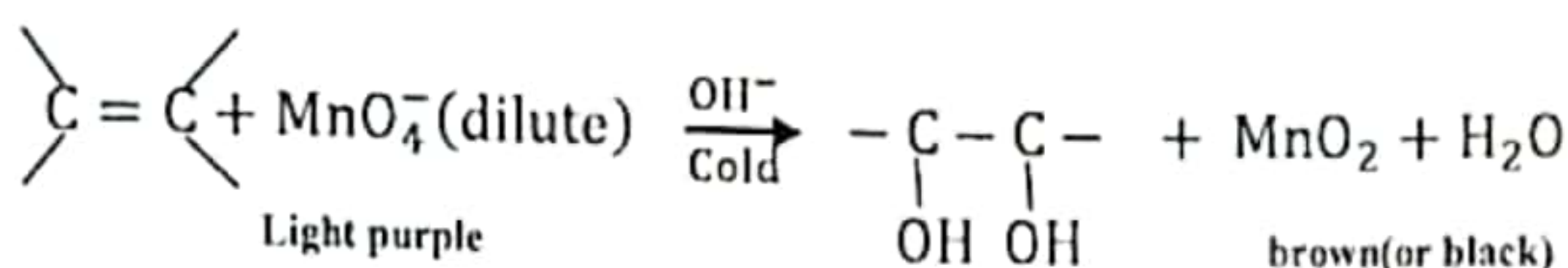
The potassium permanganate test is very useful test of different organic compounds listed below.

(i) **Unsaturated aliphatic organic compounds**

Unsaturated aliphatic organic compounds gives positive potassium permanganate test by decolourising purple colouration of the bromine.

- When potassium permanganate is used to test presence of unsaturation in the organic compound, the test is known as **Baeyer test** (in honour of Von Baeyer).
- For compounds with $C = C$, common associated conditions for the test are presence of:
 - Alkaline solution
 - Dilute ($KMnO_4$ is diluted)
 - Cold ($KMnO_4$ is cold)

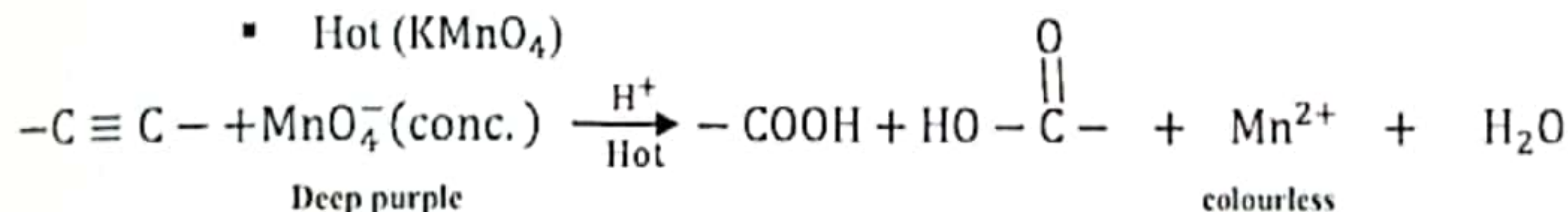
(Note: Even hot concentrated $KMnO_4$ may react with alkene and therefore decolourising the $KMnO_4$, but its more economical to use cold dilute $KMnO_4$).



In words:

Compounds with $C = C$ decolourise purple colouration of cold, dilute, alkaline $KMnO_4$ and brown (or black) colouration of MnO_2 is observed.

- For compounds with $C \equiv C$, associated conditions for the test are presence of:
 - Acidic solution
 - Concentrated ($KMnO_4$)
 - Hot ($KMnO_4$)



(Note: in this case, purple colouration of $KMnO_4$ is decolourised and **colourless** solution is observed)

It should be remembered that:

Under alkaline medium, $KMnO_4$ is reduced to MnO_2 which appears as brown (or black) while in acidic medium it is reduced to Mn^{2+} which is colourless.

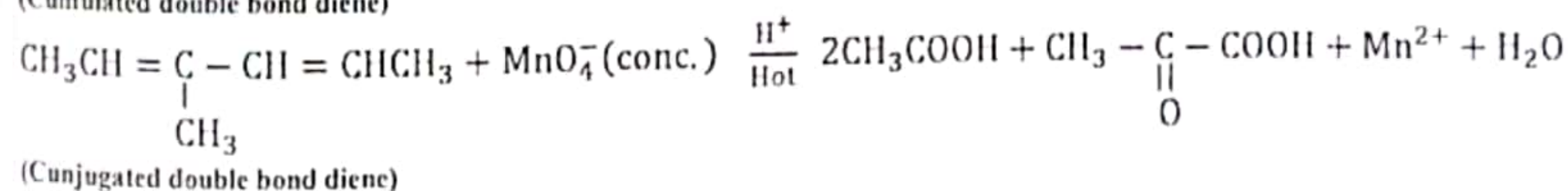
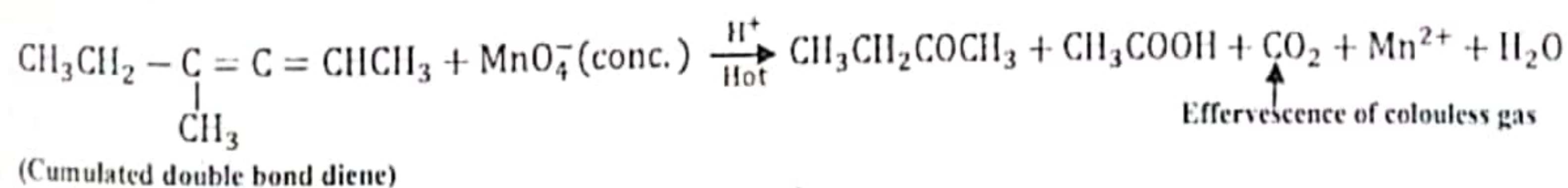
Question: Explain the chemical test you would use to differentiate hexene from benzene

(ii) **Cumulated double bond dienes**

With hot, concentrated, acidified $KMnO_4$ cumulated double bond diene give effervescence of colourless gas (CO_2) which turns lime water milky.

- So the potassium permanganate test is also very useful in distinguishing cumulated double bond diene from conjugated or isolated double bond dienes.

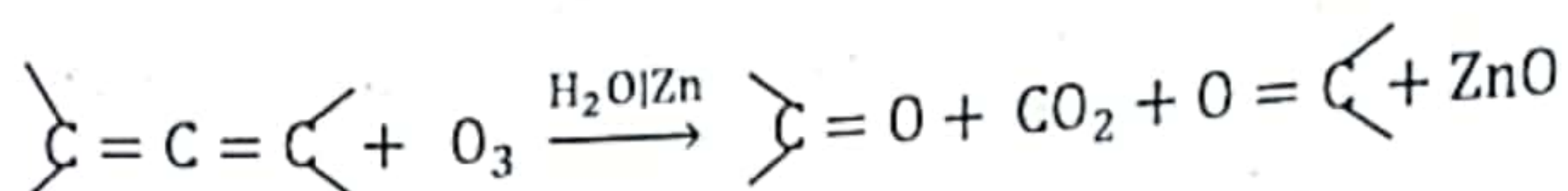
For example:



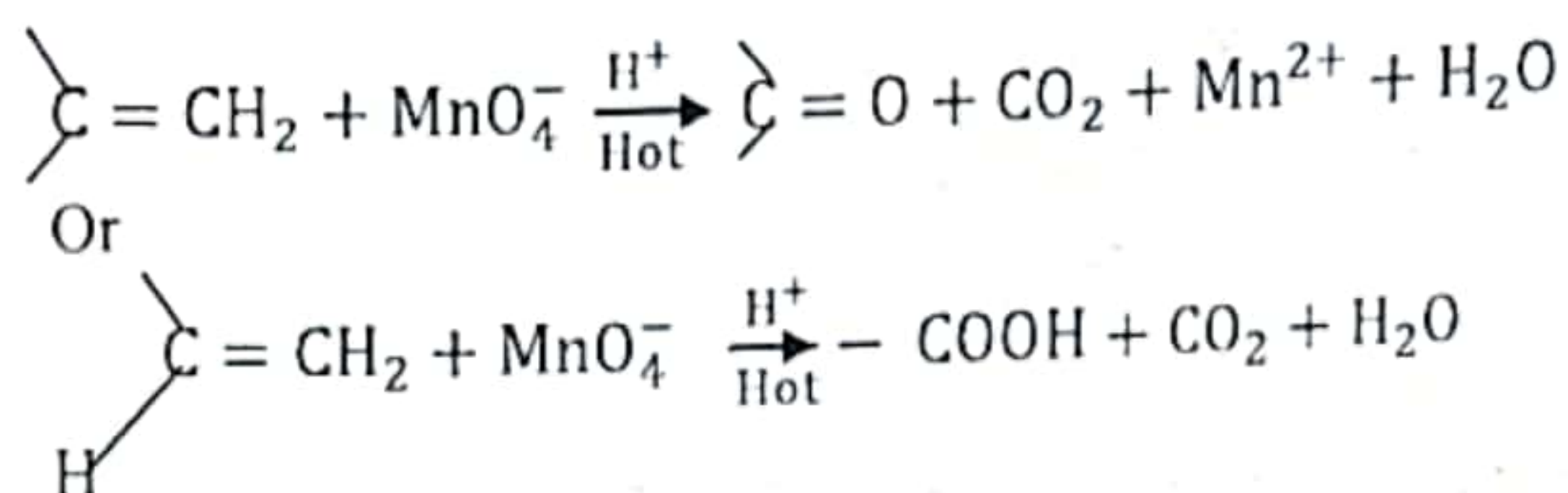
Question

With the help of chemical equation, explain how would you distinguish hepta - 2,3 - diene from hepta - 2,5 - diene.

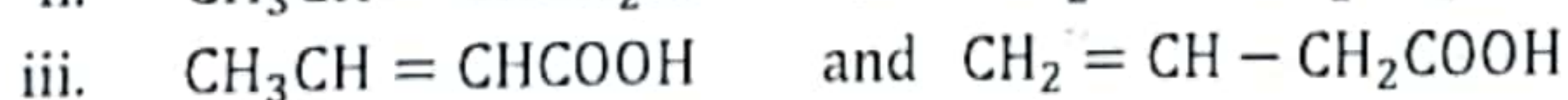
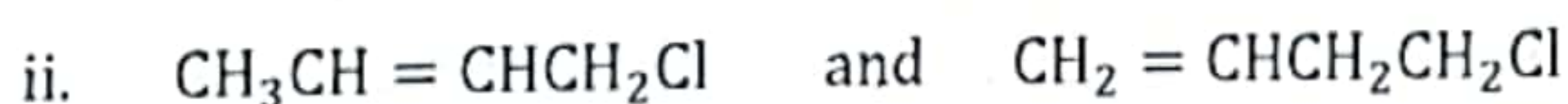
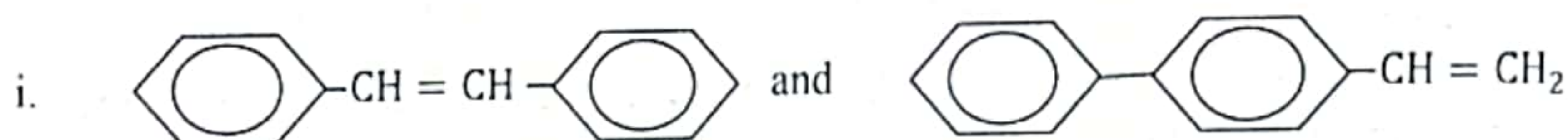
It should be understood that:
Ozonolysis reaction can also be used for the same purpose of detecting presence of cumulated double bond in diene.



With hot, concentrated, acidified KMnO_4 compound with terminal $\text{C}=\text{C}$, give effervescence of colourless gas (CO_2) which turns lime water milky.



How would you distinguish the following pairs of organic compounds:



Alkylbenzenes decolourises purple colouration of acidified potassium permanganate giving benzoic acid.

$$\text{C}_6\text{H}_5\text{R} + \text{KMnO}_4 \xrightarrow{\text{H}^+} \text{C}_6\text{H}_5\text{COOH}$$

Purple

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{MnO}_4^- \xrightarrow{\text{H}^+} \text{C}_6\text{H}_5\text{COOH} + \text{CO}_2 + \text{Mn}^{2+} + \text{H}_2\text{O}$$

Purple colourless

Question

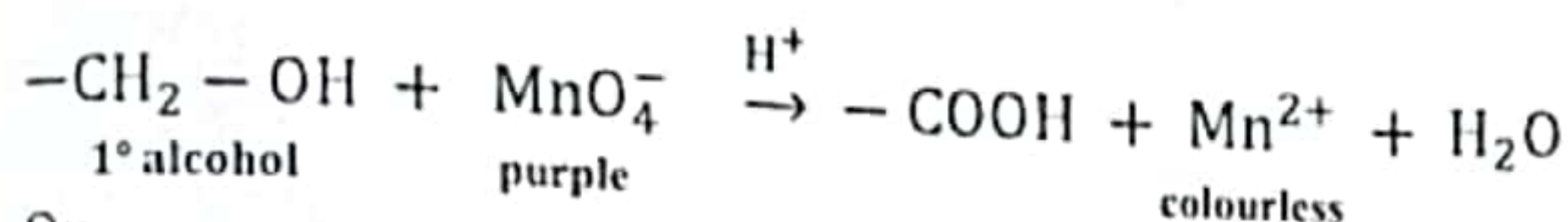
How would you distinguish:

- (i) Toluene from benzene
- (ii) Propylbenzene from propane

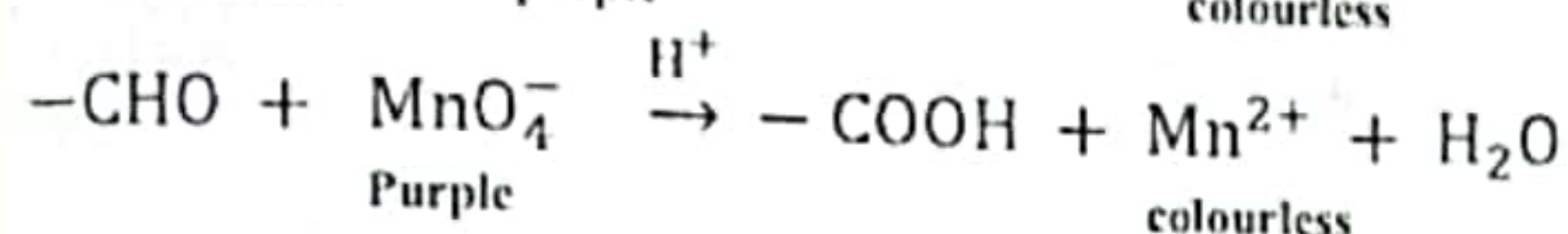
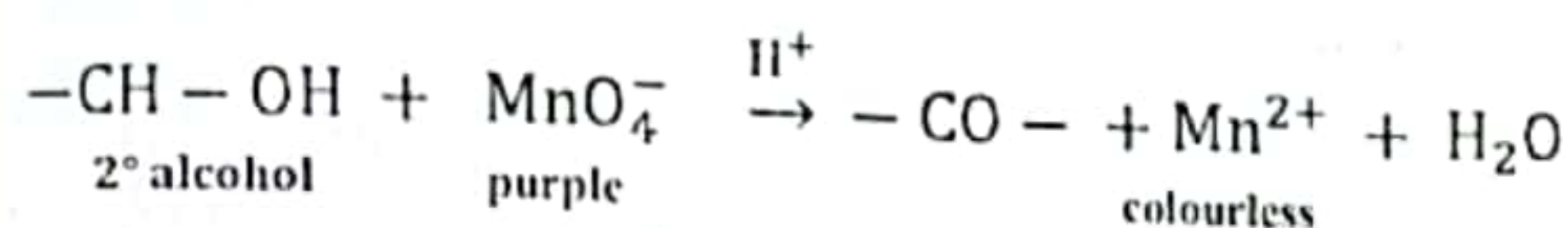
(Note: In the above equation, R not necessary to be alkyl group, even alkenyl and alkynyl give the same result)

(v) Alcohols and aldehydes

Both alcohols (primary and secondary alcohols only) and aldehyde decolourise purple colouration of acidified KMnO_4 .

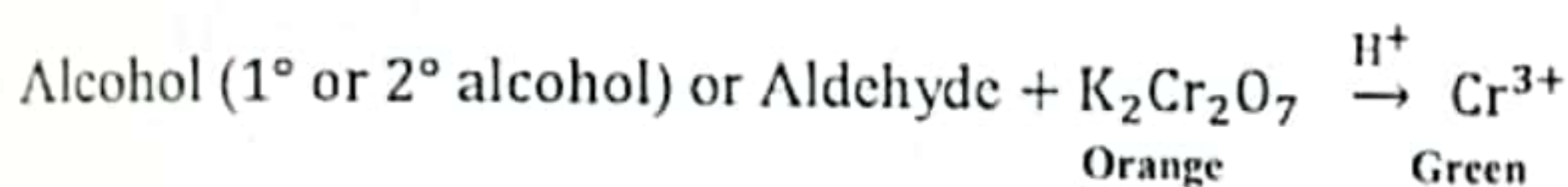


Or



It should be understood that

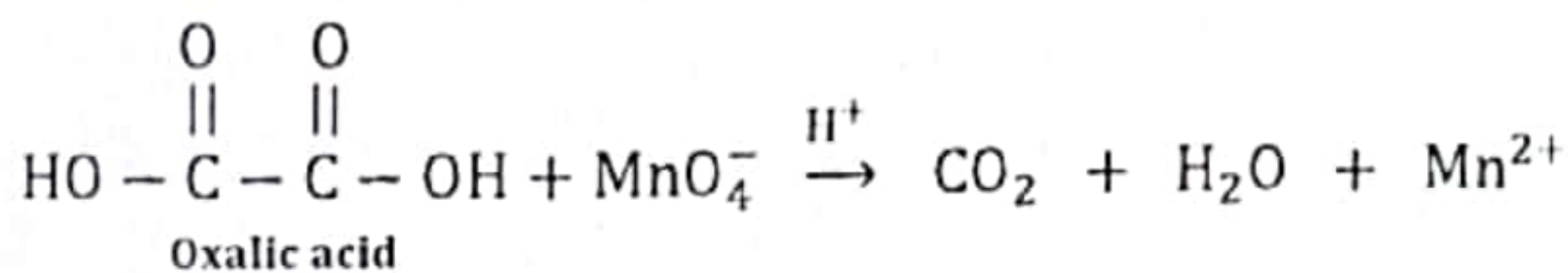
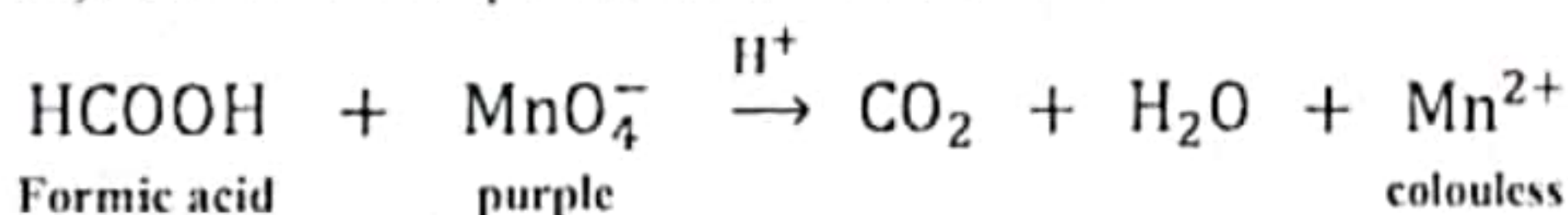
Alcohol and phenol also decolourise orange colouration of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to form green colouration of Cr^{3+} . The test is common known as **chromic acid test** because under acidic condition, $\text{K}_2\text{Cr}_2\text{O}_7$ tends to form chromic acid.



(vi) Methanoic acid and ethanedioic acid

Methanoic acid (common name is formic acid) and ethanedioic acid (common name is oxalic acid) decolourise purple colouration of acidified potassium permanganate

- Methanoic acid decolourises the permanganate at just room temperature while oxalic acid (ethanedioic acid) needs KMnO_4 to be heated to 70°C .



(Commonly written as $\text{H}_2\text{C}_2\text{O}_4$)

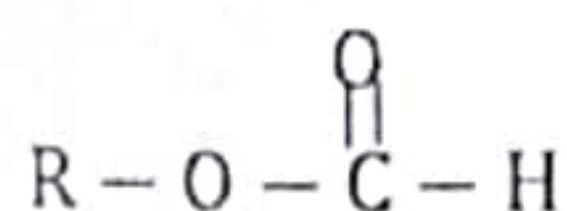
Question

How would you distinguish between:

- i. Ethanoic acid and ethanedioic acid
- ii. Methanoic acid and propanoic acid

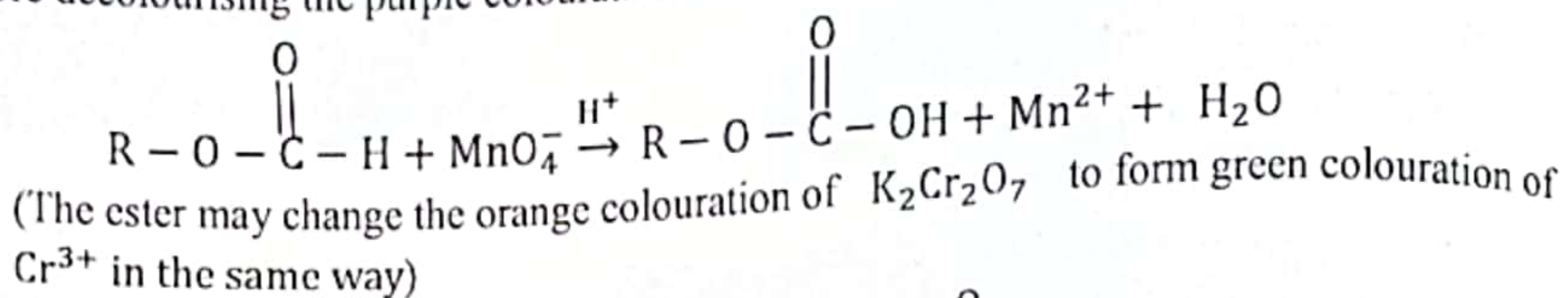
(vii) Ester with terminal carbonyl group

These are esters of this nature;



- They are methyl alkanoate.

Since they have replaceable hydrogen like aldehyde, they can be oxidised by acidified KMnO_4 and therefore decolourising the purple colouration of the permanganate.

**Question**

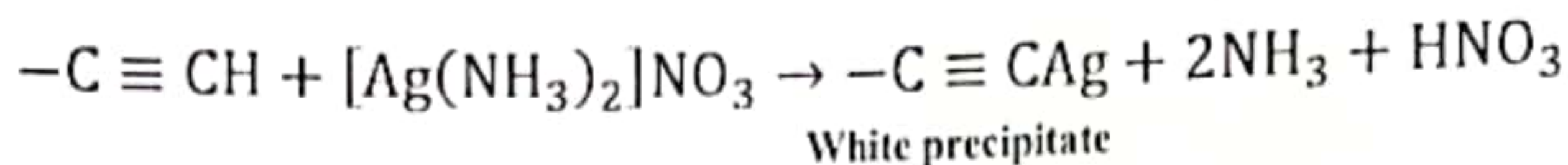
How would you distinguish $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ from $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$

Ammonical silver and copper (I) salt tests

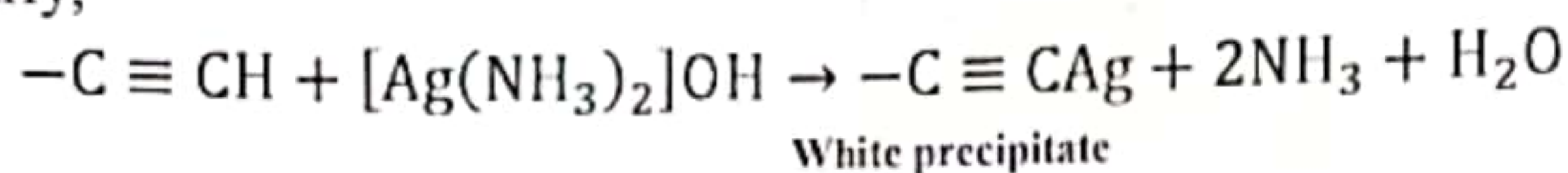
These are tests of presence of terminal $\text{C} \equiv \text{C}$ in the compound.

For Ammonical silver salt test:

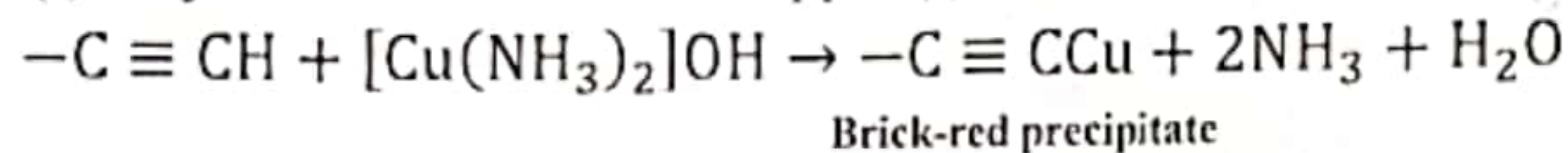
Compounds with terminal $\text{C} \equiv \text{C}$, gives white precipitate of silver alkynide with Ammonical silver salt.



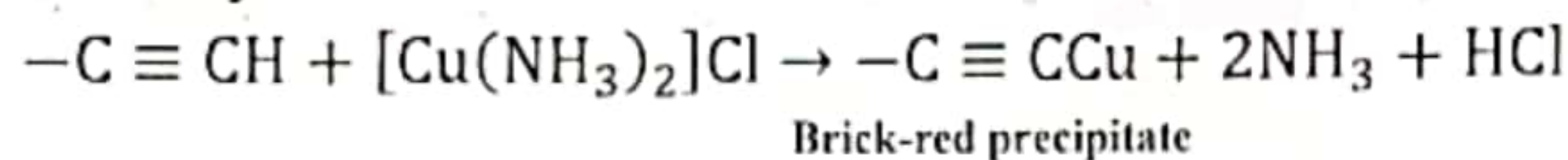
Similarly;

**For Ammonical copper (I) salt test:**

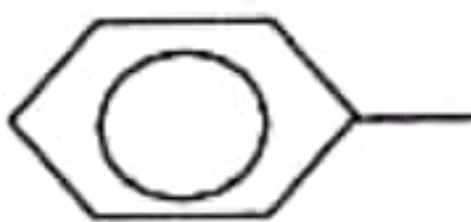
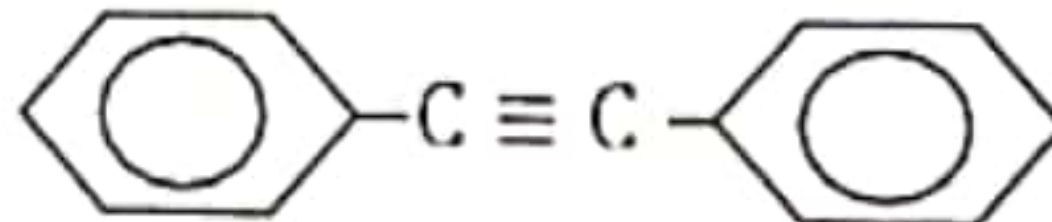
Compounds with terminal $\text{C} \equiv \text{C}$, give brick red precipitate of copper (I) alkynide with Ammonical copper (I) alkynide with ammonical copper (I) salt.



Similarly

**Question**

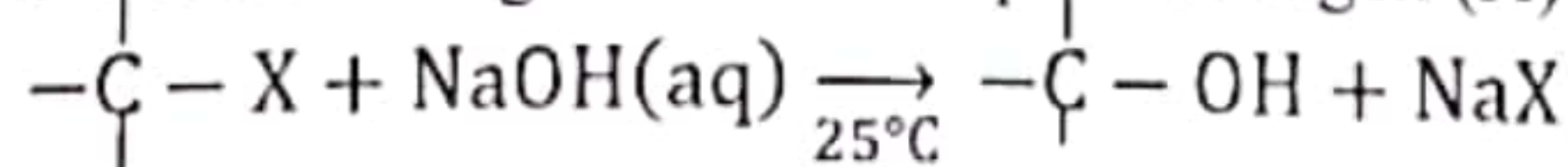
Give test to distinguish the following pair of organic compounds:

- (i) Propyne and but-2-yne
- (ii) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{C} \equiv \text{CCH}_3$ and $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\text{C} \equiv \text{CH}$
- (iii)  $\text{C} \equiv \text{CH}$ and  $\text{C} \equiv \text{C}$

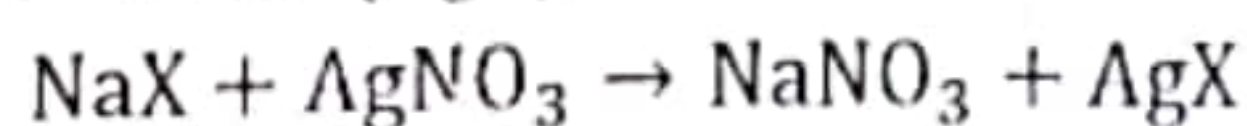
NaOH followed by $\text{AgNO}_3(\text{aq})$ test

This is very useful test for detecting presence of substitutable halogen in the organic compounds.

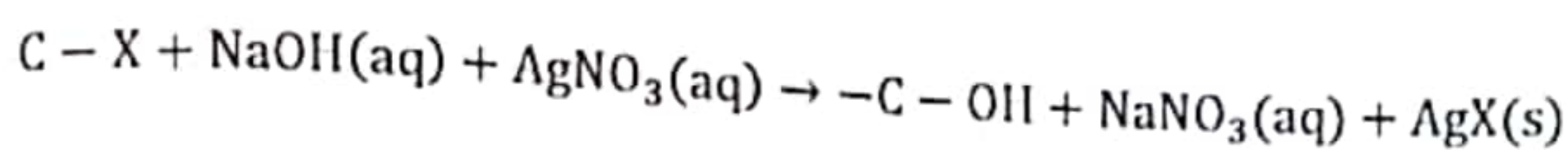
– The aim of introducing NaOH is to replace halogen (X) in nucleophilic substitution reaction.



– The aim of adding $\text{AgNO}_3(\text{aq})$ to detect presence of halogen in the compound by precipitating silver halide (AgX)



And the overall reaction becomes;

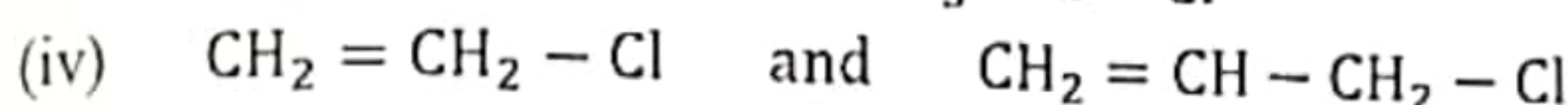
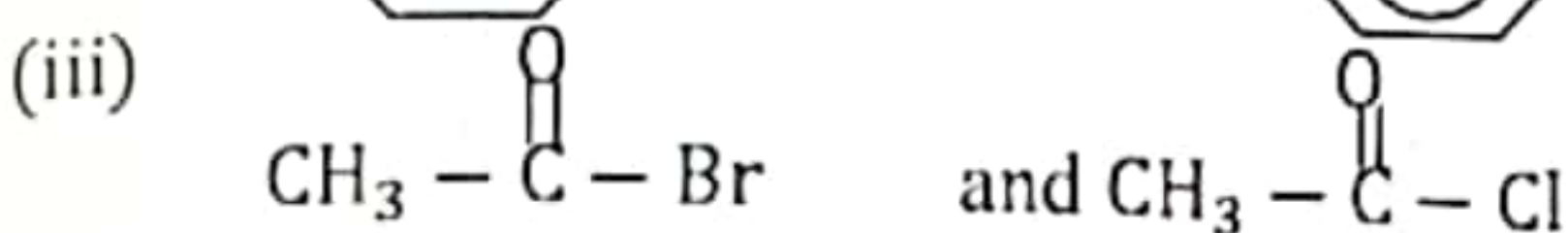
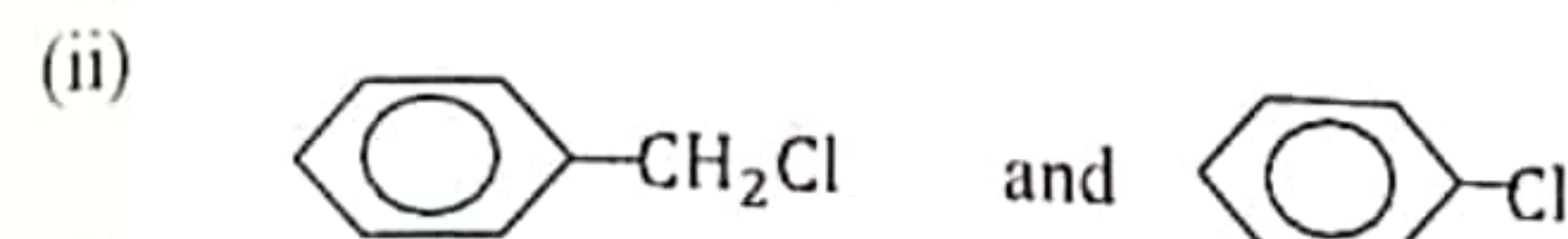
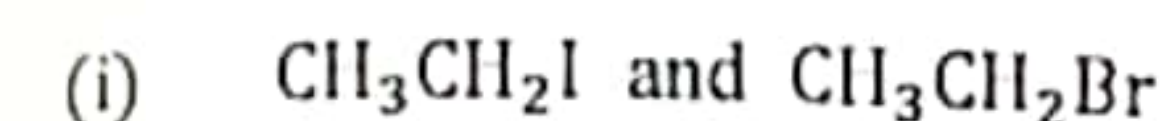


If X is:

- Cl, white precipitate of AgCl will be observed.
- The AgCl formed is soluble in aqueous ammonia, $NH_3(aq)$
- Br, light yellow precipitate of AgBr will be observed
- The AgBr formed partially soluble in aqueous ammonia, $NH_3(aq)$
- I, deep yellow precipitate of AgI will be observed
- The AgI formed is insoluble in $NH_3(aq)$

Question

Describe how you would distinguish the following pair of organic compounds

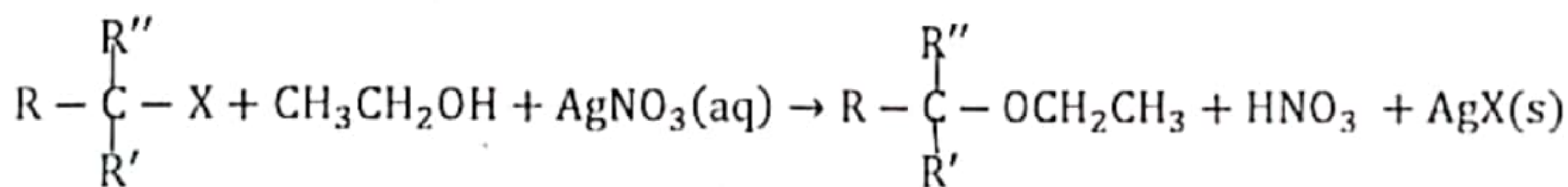


Alcoholic $AgNO_3(aq)$ test

This is very useful test for measuring rate of haloalkane in nucleophilic substitution reaction.

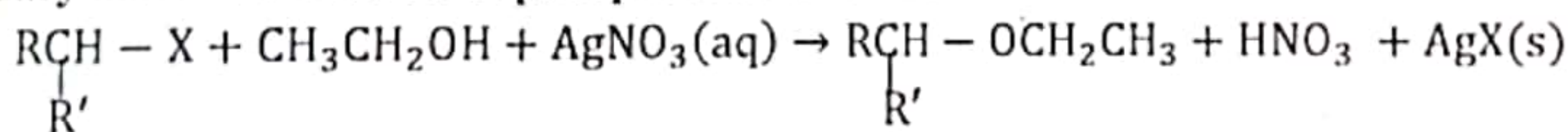
- So its very useful in differentiating primary, secondary and tertiary haloalkane by measuring the time taken by haloalkane to form complete precipitate of silver halide.

Tertiary haloalkane being most reactive, forms the precipitate immediately.



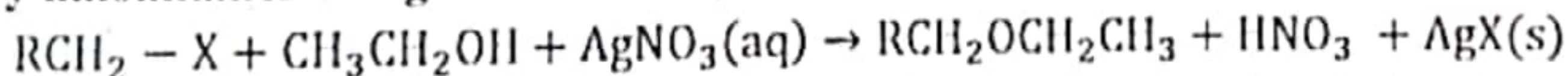
(Here the precipitate AgX is formed immediately)

Secondary haloalkane forms the precipitate after few seconds



(Here the precipitate of AgX is formed after few seconds)

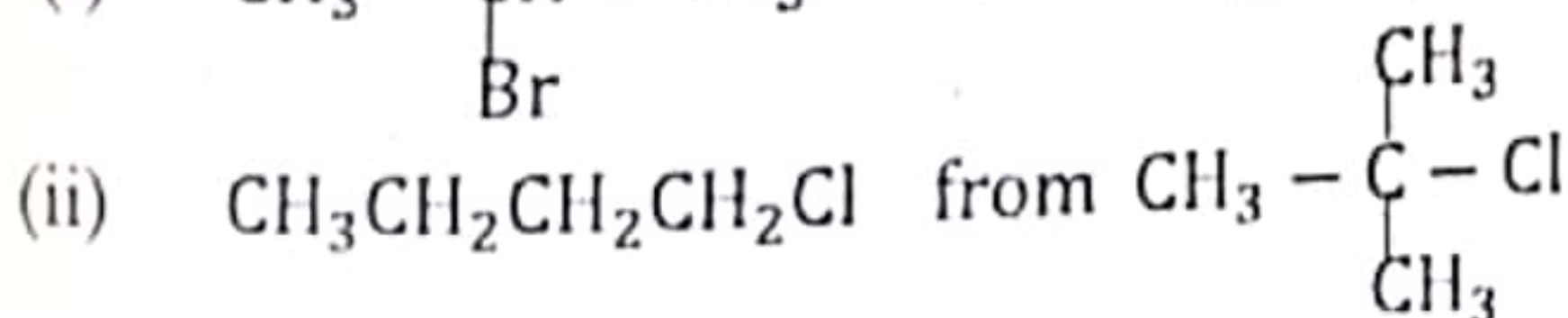
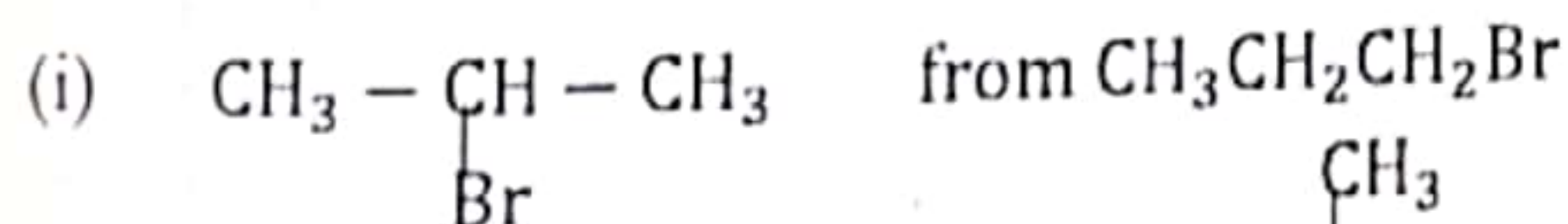
Primary haloalkanes being least reactive, take longer time to form the precipite of AgX



(Here it may take some minutes for precipitate of AgX to be observed)

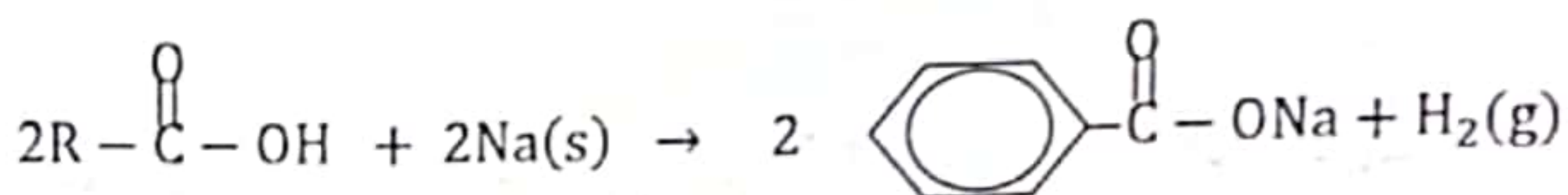
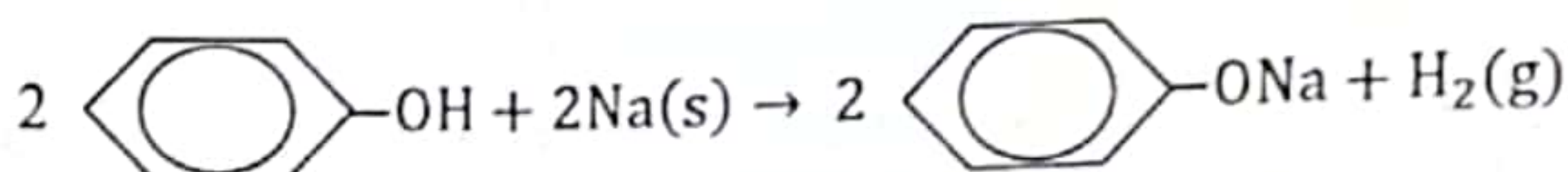
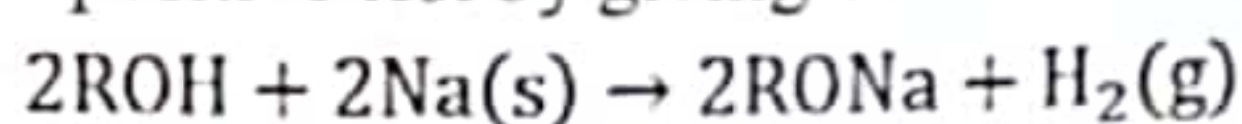
Question

How would you distinguish:



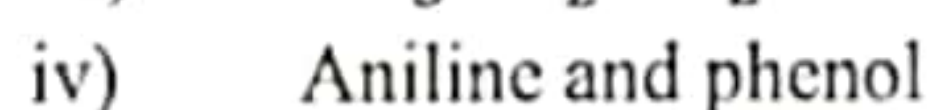
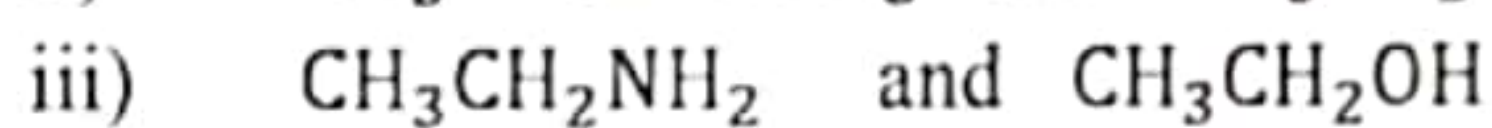
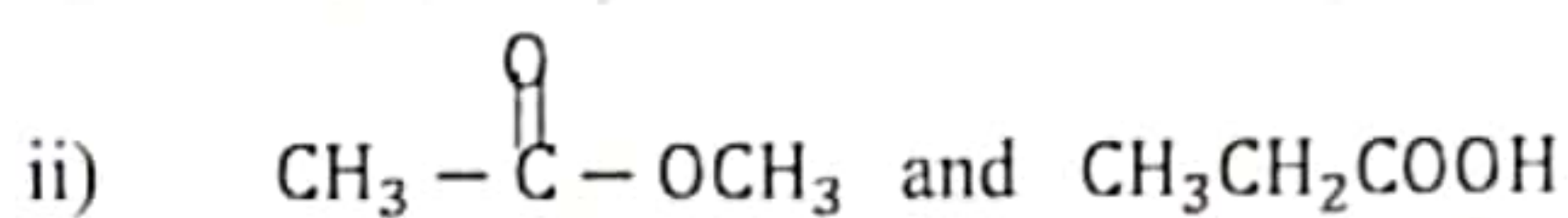
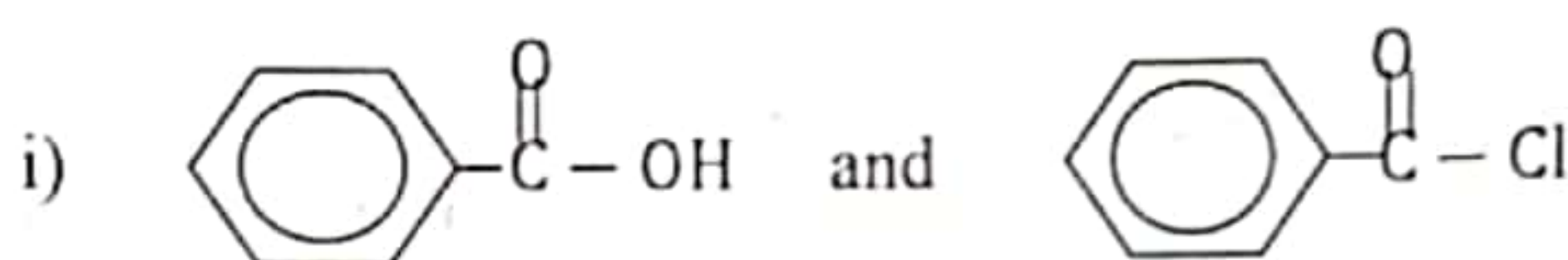
Sodium metal is the for alcohols, phenols and carboxylic acid.

- They give positive test by giving brisk effervescence of hydrogen gas with the metal



Question

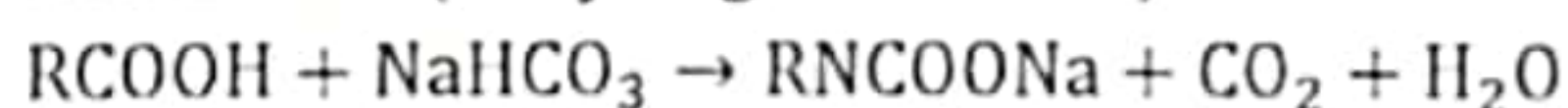
Give chemical tests to do distinction of the following pairs of organic compounds:



Sodium bicarbonate test

This is the test for carboxylic acids

- Carboxylic acids give positive sodium bicarbonate test by giving effervescence of colourless gas which turns lime water milky; that is CO_2 is evolved on the reaction between carboxylic acid and sodium bicarbonate (or hydrogencarbonate).



Question

Give a chemical test to distinguish between phenol and benzoic acid.

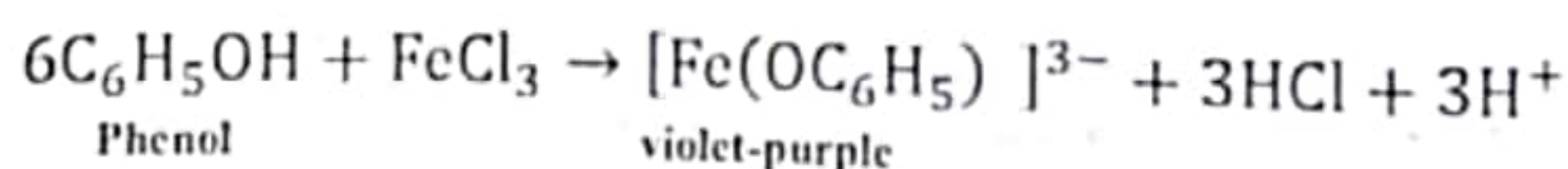
Ferric chloride test

Ferric chloride is the common name of iron (III) chloride FeCl_3 .

- The ferric chloride test is the useful test of phenol and carboxylic acids

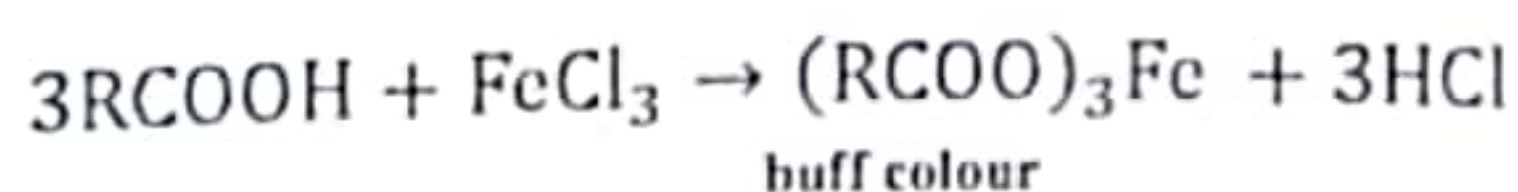
For phenol:

Phenol gives positive ferric chloride test by forming violet-purple complex



For carboxylic acid:

Carboxylic acids give positive ferric chloride test by giving buff coloured (yellowish-brown) compound



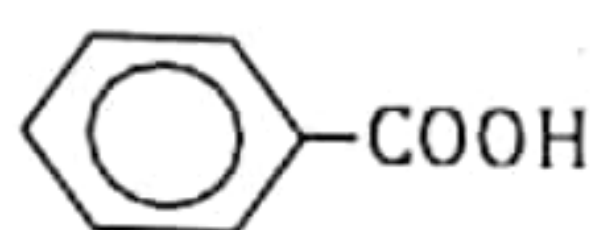
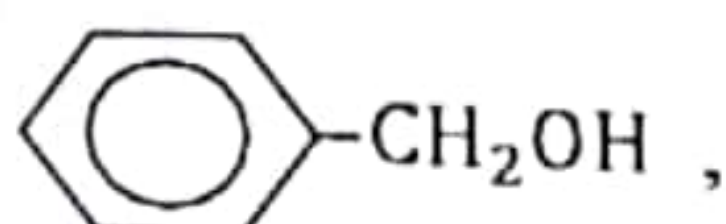
The reader should understand that:

Alcohol (another compound with OH group like phenol and carboxylic acid give negative test with ferric chloride as there is no chemical reaction between alcohol and FeCl_3 .

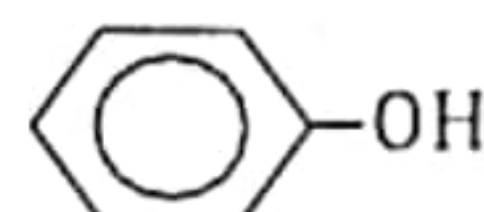
- So the ferric chloride test is very important in distinguishing alcohol, phenol and carboxylic acid.

Question

With the help of chemical equations explain the chemical test you would use to distinguish the following compounds:



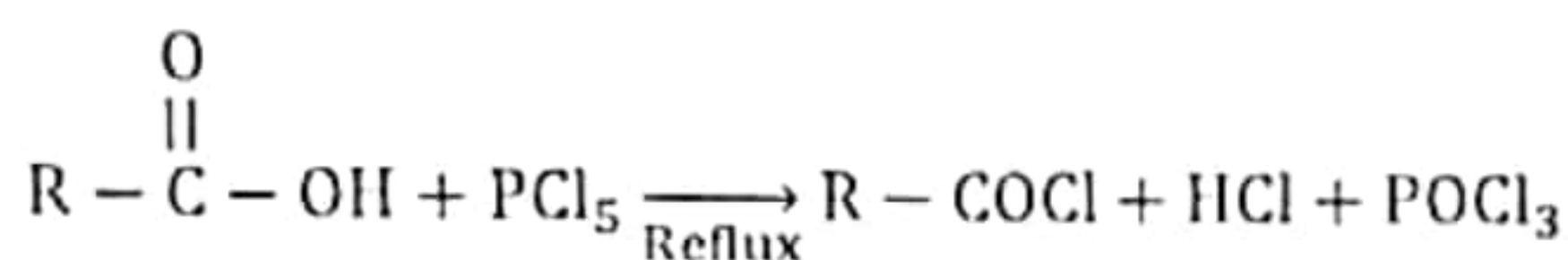
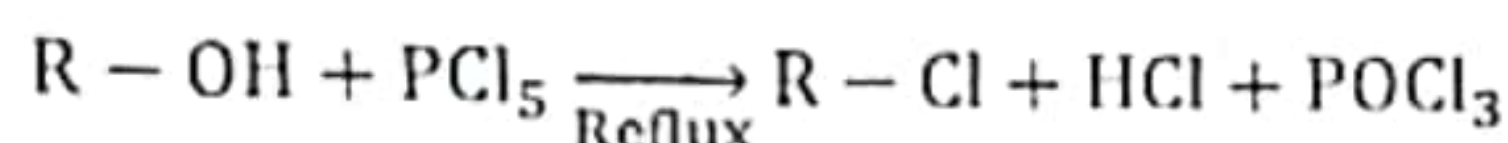
and



Phosphorus pentachloride test

This is the useful test of presence of OH group in the organic compounds.

- Alcohols and carboxylic acids give positive phosphorous pentachloride by giving white fumes (misty fumes) of hydrogen chloride gas with the PCl_5 . The gas produce dense white fumes with ammonia.



Question

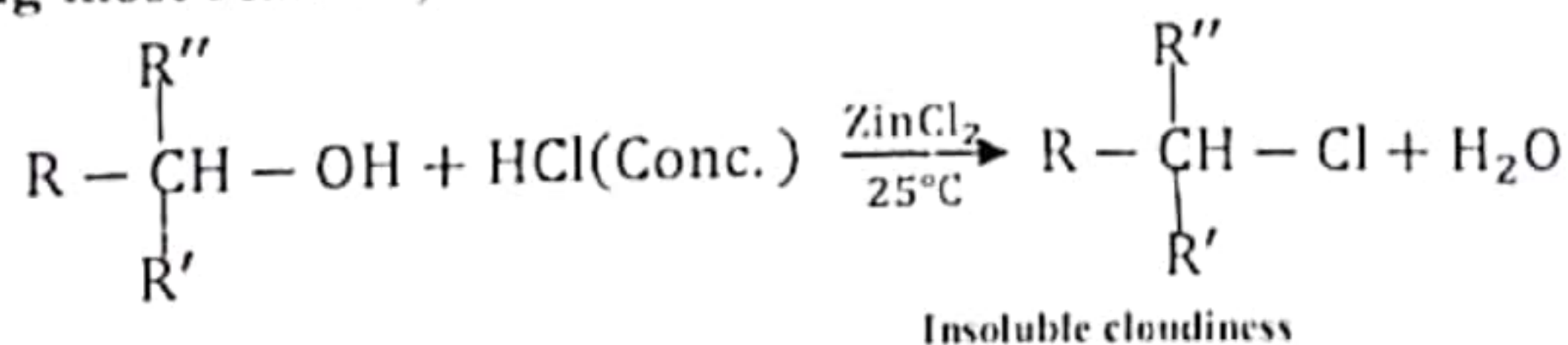
How would you distinguish between ethanal and ethanol? (Remember! Even aldehydes and ketone react with PCl_5 ; the only difference is that aldehydes and ketone do not evolve HCl(g))

Lucas test

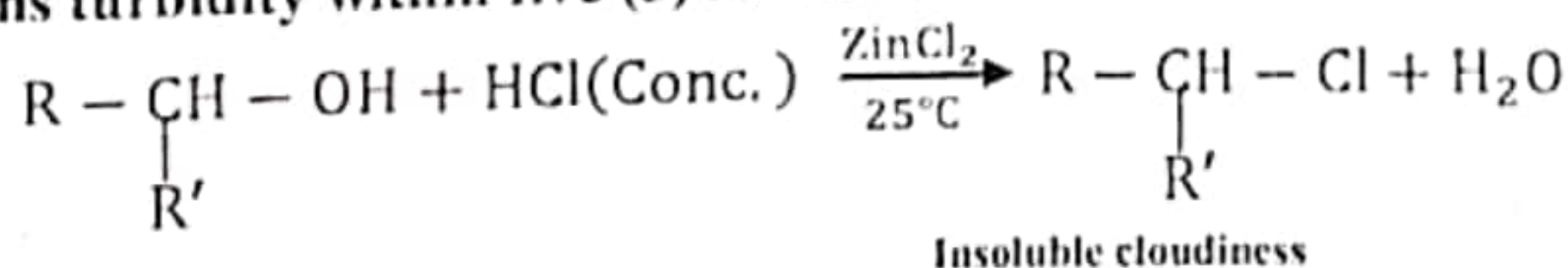
This is very useful test for measuring rate of alcohols in nucleophilic substitution reaction.

- So it is very useful in differentiating primary, secondary and tertiary alcohol by recording the time taken by alcohol to form turbidity (insoluble cloudiness).
- It employs Lucas reagent which is the mixture of concentrated hydrochloric acid and zinc chloride mixed at equal proportion.

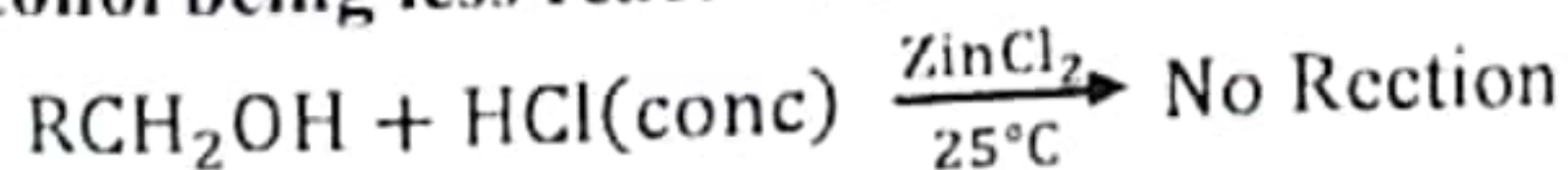
Tertiary alcohol being most reactive, forms the turbidity immediately.



Secondary alcohol forms turbidity within five (5) minutes.

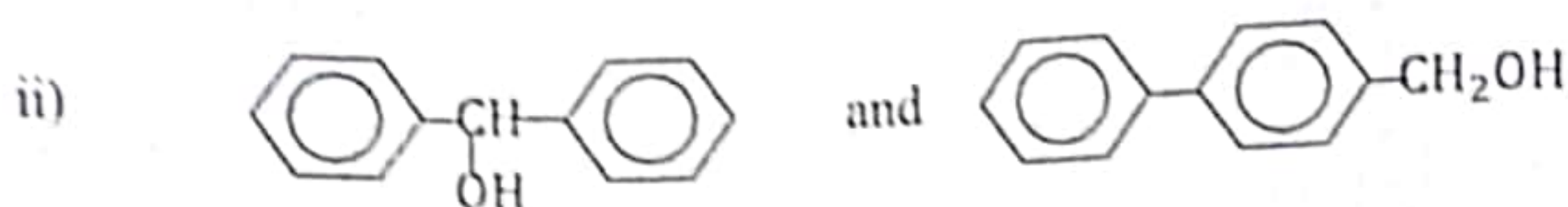
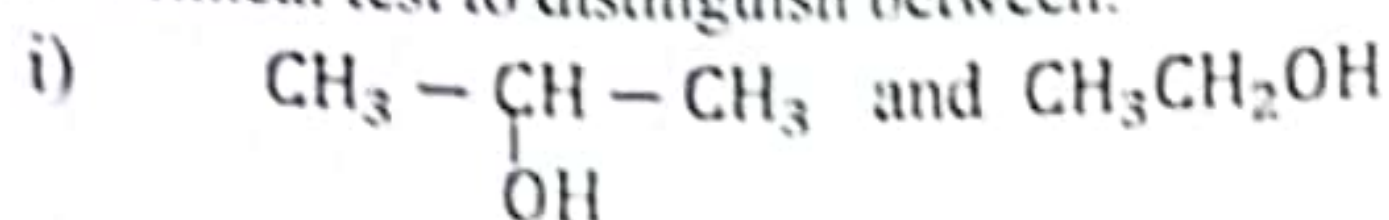


Primary alcohol being less reactive does not form turbidity. (Actually, it can form after few days)



Question

Give chemical test to distinguish between:

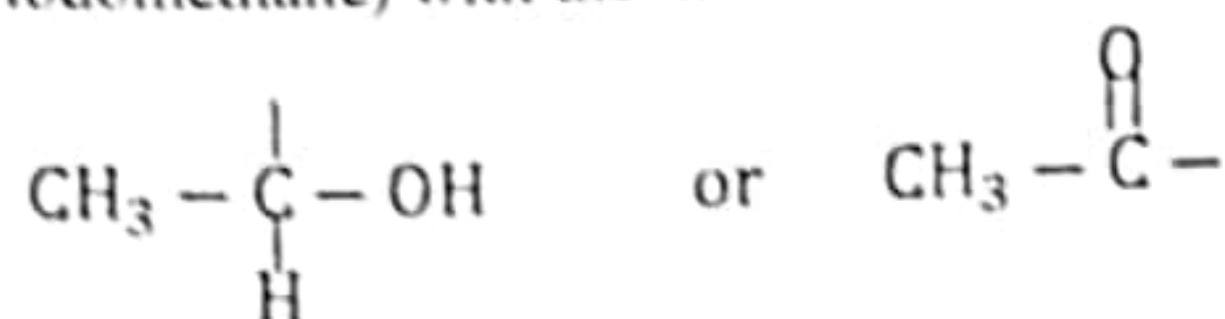


Iodoform test (Triiodomethane test)

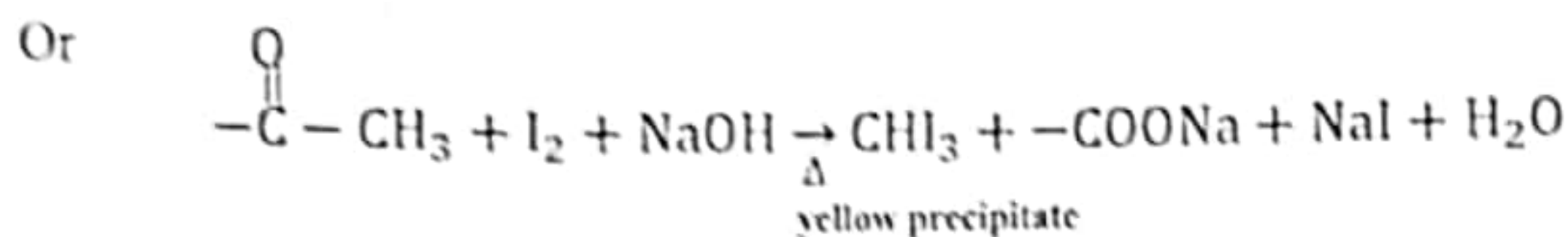
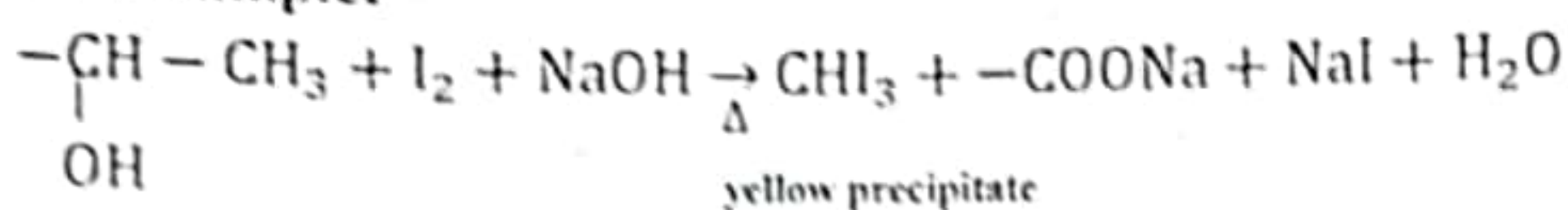
This is the test of presence of terminal methyl group bonded to either OH group of 1°

and 2° alcohol or carbonyl group $\left(\overset{\text{O}}{\parallel} \text{C} - \right)$ of aldehyde and ketone.

- Therefore compounds with these group gives positive iodoform test by giving yellow precipitate of CHI_3 (iodoform or triiodomethane) with the mixture of I_2 and NaOH .



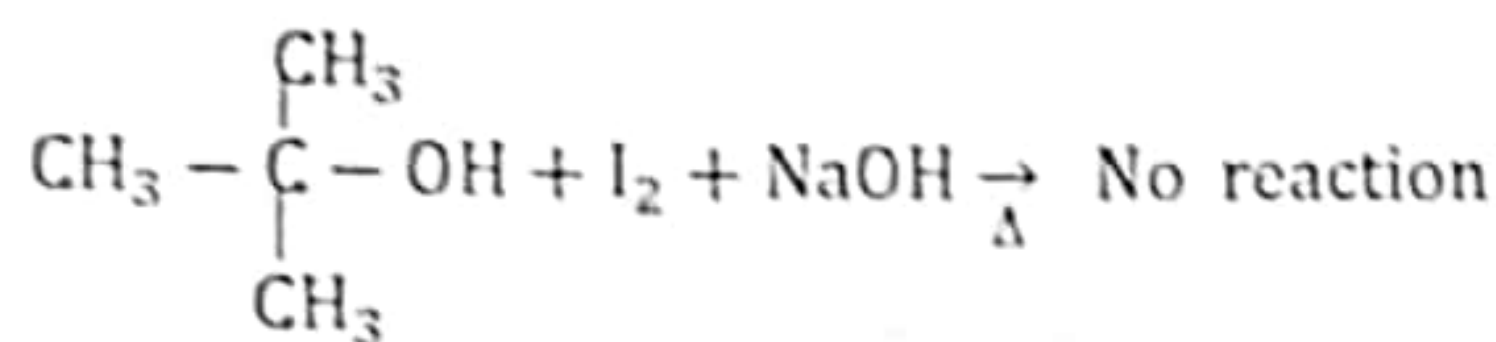
For example:



Warning!

Tertiary alcohol does not give positive iodoform test even if it has the terminal methyl group because in alcohols the iodoform reaction takes place via oxidation mechanism and tertiary alcohols resist oxidation reaction (there is no replaceable hydrogen in tertiary alcohol).

For example:



Question

Explain chemical tests to distinguish the following pairs of organic compound

- Ethanol and propanol
- Pentan-3-ol and butan-2-ol

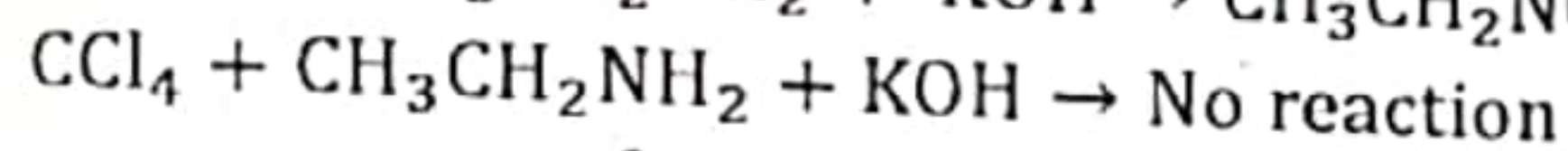
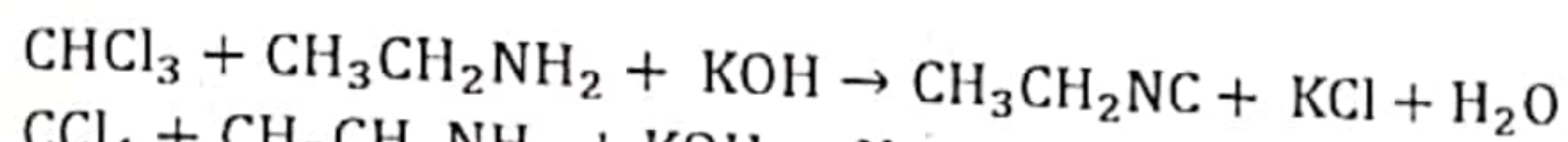
Since chloroform is an organic compound too we can use primary amine to test presence of chloroform in organic chemistry.

Example 1

With the help of chemical equations, give a chemical test to distinguish between chloroform (CHCl_3) and carbon tetrachloride (CCl_4).

Solution

With primary amine like ethanamine under alkaline solution like KOH, CHCl_3 gives offensive smell of carbylamine **while** CCl_4 does not.



(Other common names of methanal are formaldehyde, formilin, formal and methylene oxide)

Tollen's reagent and Fehling's solution test

These tests are useful for aldehyde and methanoic acid.

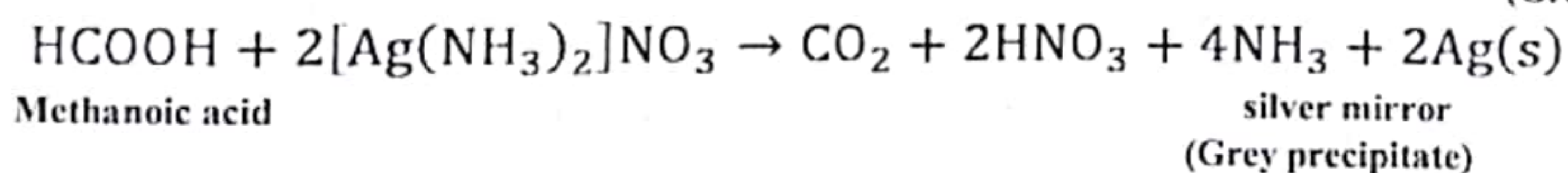
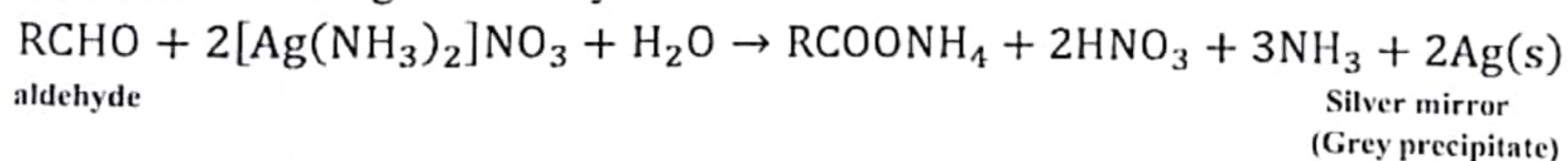
For Tollen's reagent test:

This is also known as silver mirror test.

- It employs ammoniacal silver nitrate, $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$ reagent which is known as Tollen's reagent. It is mild oxidizing agent.

Both aldehyde and methanoic acid give positive Tollen's reagent test by forming silver (grey) precipitate which appears as the silver mirror in the test tube and hence the term '**silver mirror test**' for the test.

- Ketone and higher member of carboxylic acids give negative test because they resist oxidation reaction. so the test is very important in distinguishing either aldehyde from ketone or methanoic acid from higher carboxylic acids.

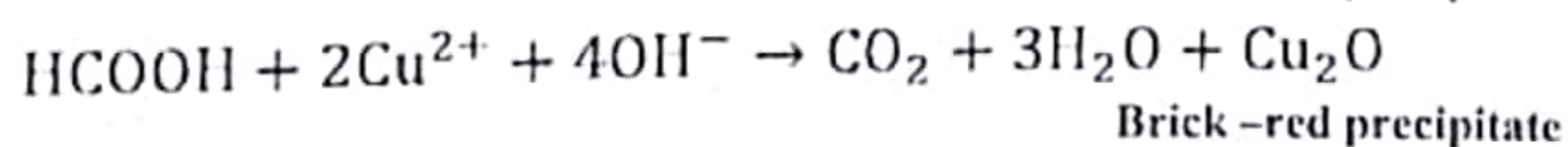
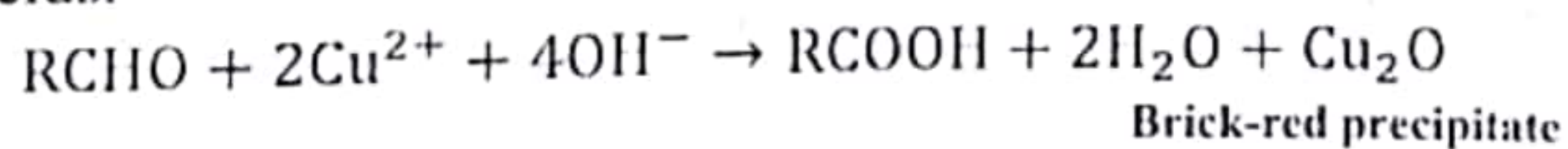
**For Fehling's solution test**

Fehling's solution is an alkaline solution containing Cu^{2+} .

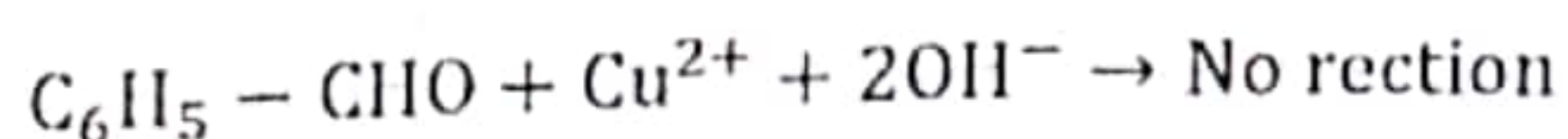
- Like Tollen's reagent it is mild oxidizing agent

Both aldehyde and methanoic give positive Fehling's solution test by giving brick-red precipitate of Cu_2O

- Ketones and higher carboxylic acids give negative test because they resist oxidation reaction. So the test is also commonly used to distinguish either aldehydes and ketones or methanoic acid and higher carboxylic acids.

**Do you remember this fact?**

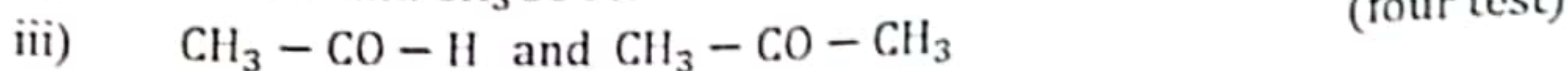
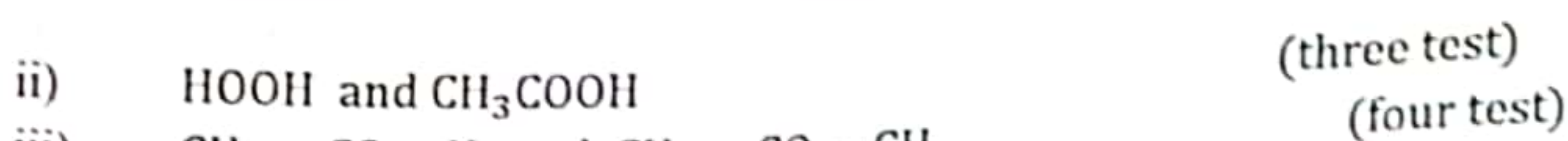
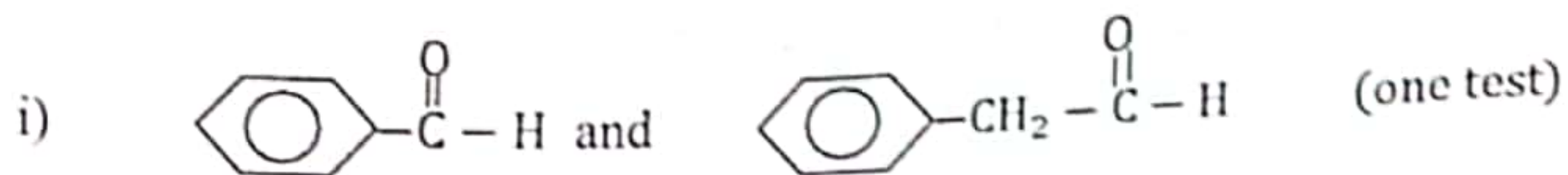
Benzaldehyde ($\text{C}_6\text{H}_5 - \text{CHO}$) is the only common aldehyde which gives negative test with Fehling's solutions.



Also the reader should remember that Benedict solution shows similar results to Fehling's solution because they both contain Cu^{2+} which will be reduced to Cu_2O by aldehyde or methanoic acid.

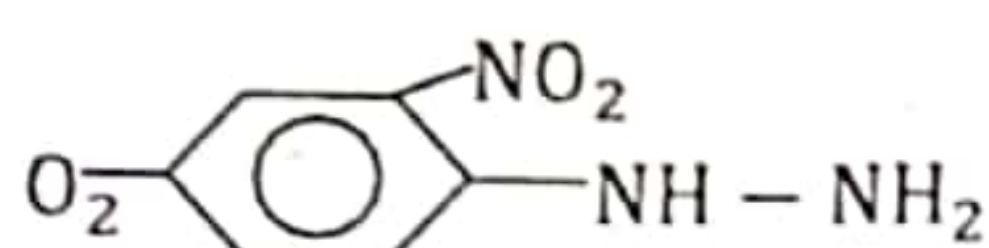
Question

Give a chemical test to distinguish the following pairs of organic compounds

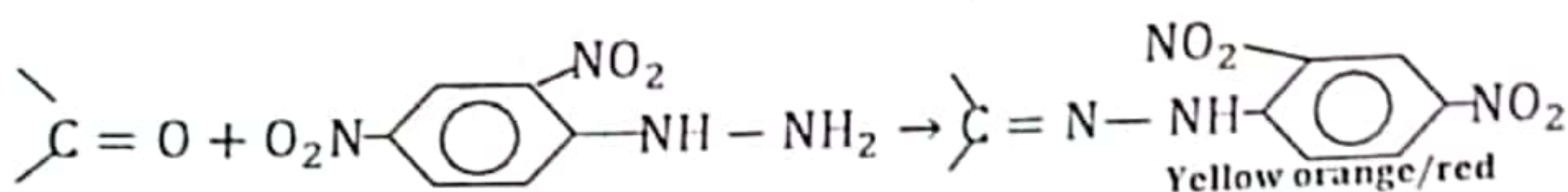


2,4 - dinitrophenylhydrazine(or Brady's reagent) test

2,4 - dinitrophenylhydrazine or Brady's reagent has the following structure:



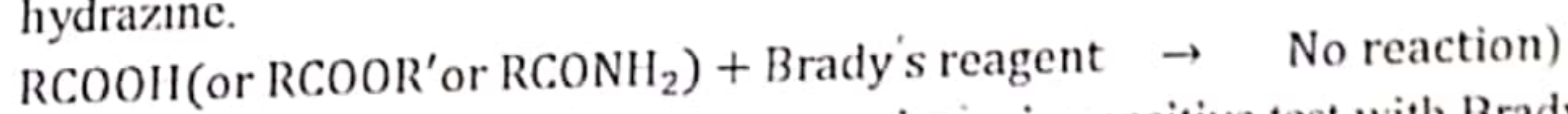
- 2,4- dinitrophenylhydrazine is commonly denoted as DNPH or simply DNP. The reagent is very useful to detect presence of carbonyl group in the organic aldehydes and ketones by giving yellow-orange precipitate of 2,4- dinitrophenylhydrazone for aliphatic carbonyl compound. But for aromatic carbonyl compound, the colour will be red.



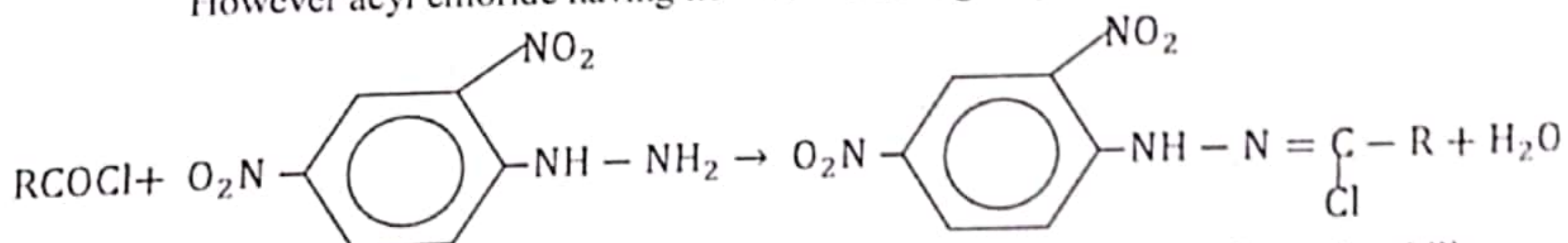
Be careful!

Although carboxylic acids and esters (and of course amide) have carbonyl group like aldehyde and ketone, they do not give positive test with Brady's reagent, why?

- This is because, delocalization of electrons (as result of mesomerism) in the carboxylic group makes the carbon in the carbonyl group of carboxylic acid (and its derivatives) less electrophilic and hence it is not subjected to the nucleophilic attack of the nitrogen in the hydrazine.



However acyl chloride having no mesomerism, give positive test with Brady's reagent



- Generally reactivity of carbonyl compounds towards nucleophile in nucleophilic substitution reaction is according to the following order:-

Acyl (or acid) halide > Acid anhydride > Aldehyde > Ketone > Carboxylic acid > Ester > Amide

(Anything below aldehyde and ketone in the series, that is carboxylic acid, ester and amide will not react with Brady's reagent due to delocalization of electrons from O or N into $\text{C}=\text{O}$).

The reader should understand that:

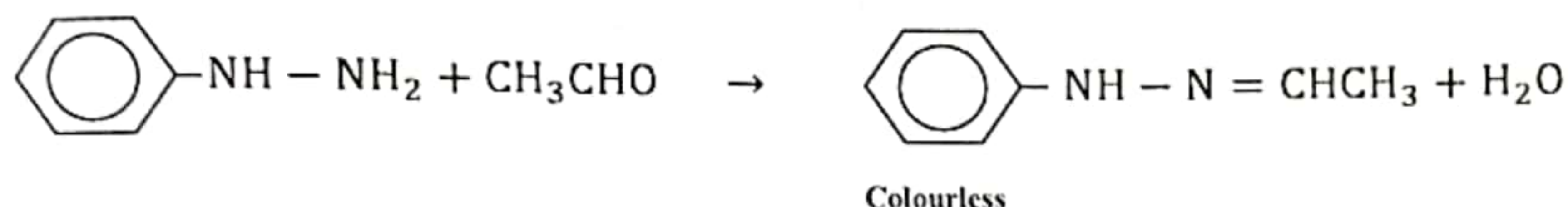
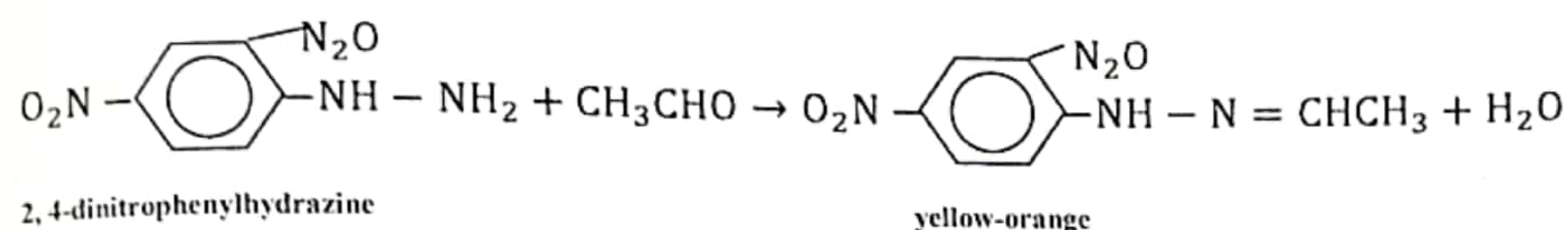
Since Brady's reagent is an organic compound too, we can use carbonyl compound to test the presence of Brady's reagent as far as organic chemistry is concerned.

Example 2

With the help of chemical equations, give a chemical test to distinguish between phenylhydrazine and 2,4-dinitrophenylhydrazine.

Solution

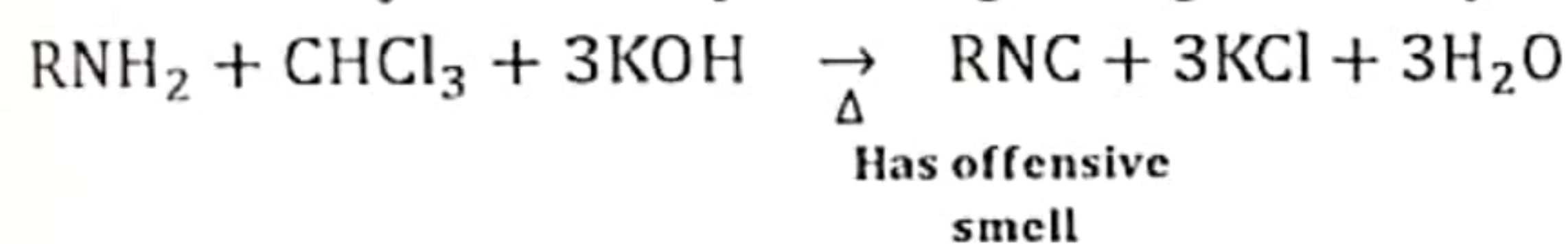
With carbonyl compound like ethanal, 2,4-dinitrophenylhydrazine gives yellow-orange precipitate while phenylhydrazine does not.



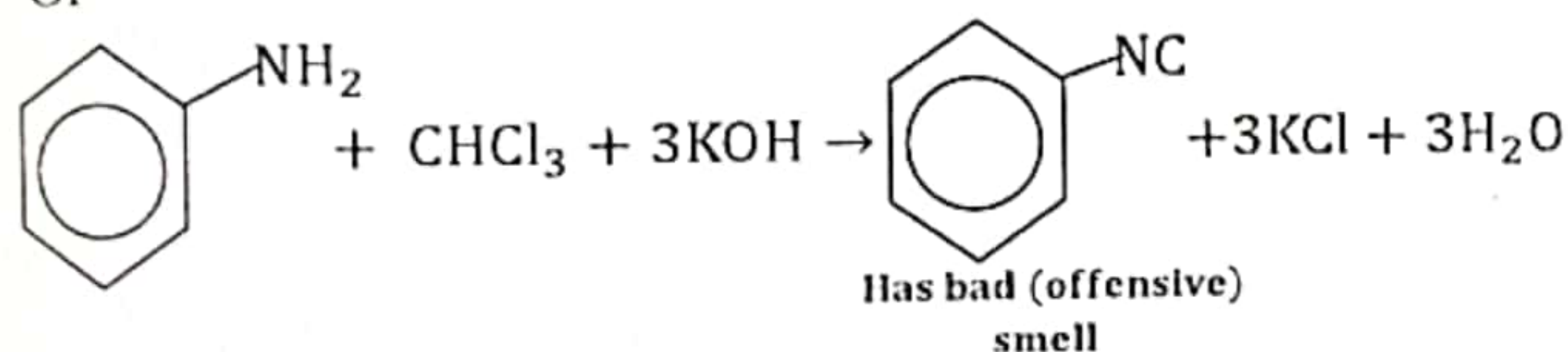
Carbylamine test (or isocyanide test)

This is very useful test for primary amine

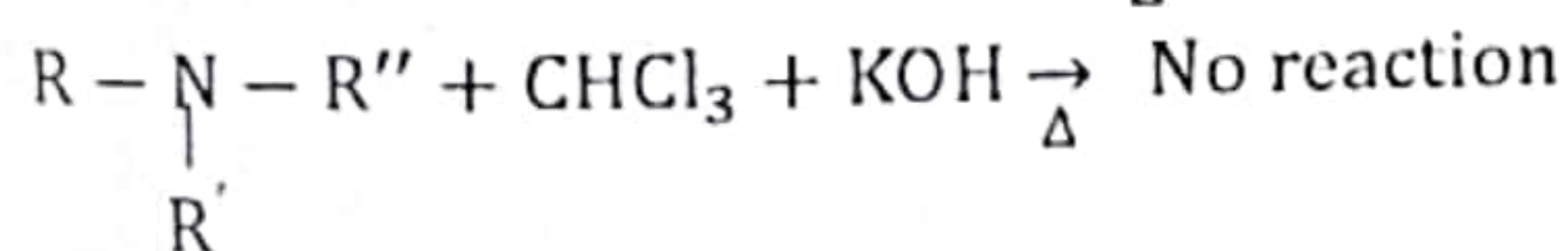
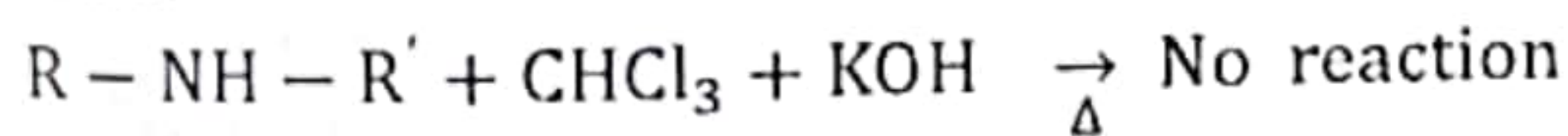
- Only primary amine give positive iodoform test by giving offensive smell of the carbylamines (hence the name carbylamine test).
- Secondary and tertiary amines give negative carbylamines test



Or



While



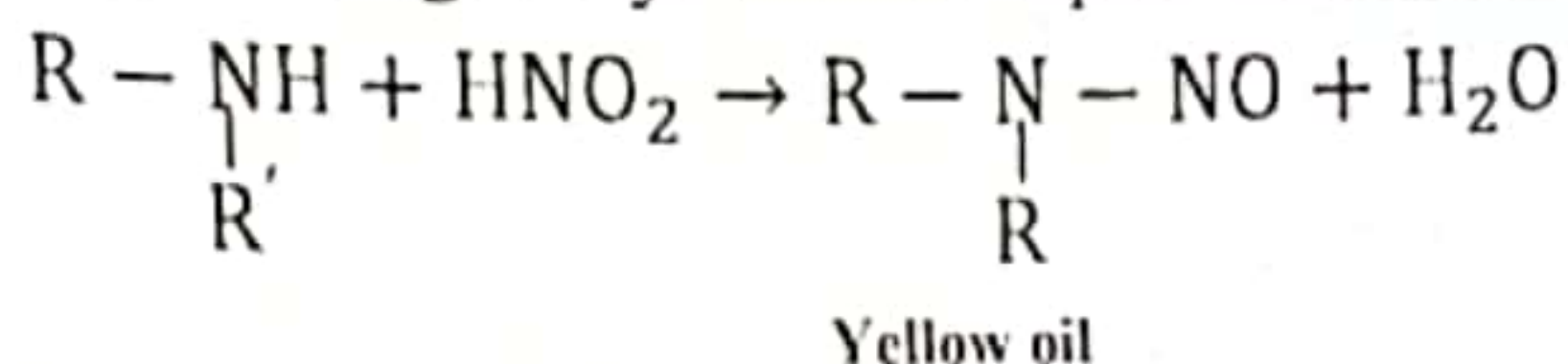
Nitrous acid (HNO₂) Test

This is useful test to distinguish between primary, secondary and tertiary amine

- Primary amine (except aniline) give colourless solution accompanied with bubbles of colourless, odourless nitrogen gas.

$\text{RNH}_2 + \text{HNO}_2 \rightarrow \text{ROH} + \text{N}_2 + \text{H}_2\text{O}$ (Aniline undergo diazotisation reaction with HNO₂ and does not give bubbles of N₂ although it also primary amine).

- Secondary amine gives yellow oil liquid of nitrosamine).

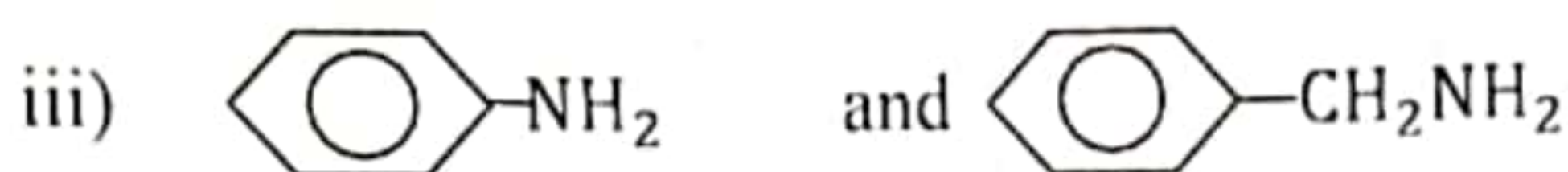
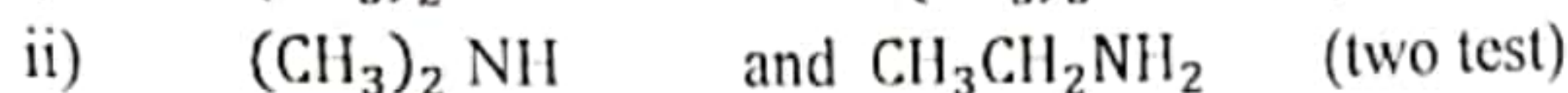
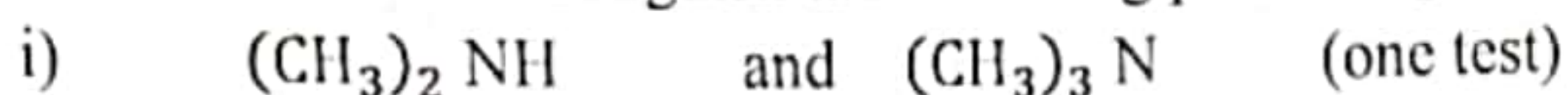


- Tertiary amine gives clear solution of trimethylammonium nitrite without evolution of any gas.



Question

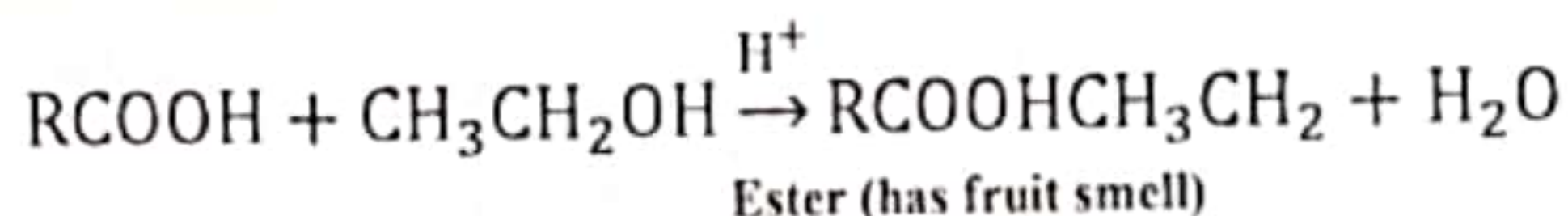
Give chemical test to distinguish the following pair of organic compound



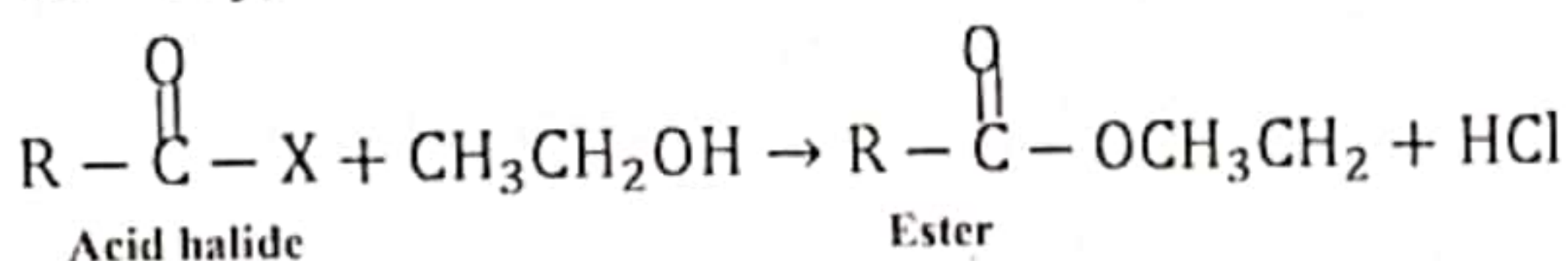
Ethanol test

This is useful test of carboxylic acid (and of course acid anhydride and acid halides).

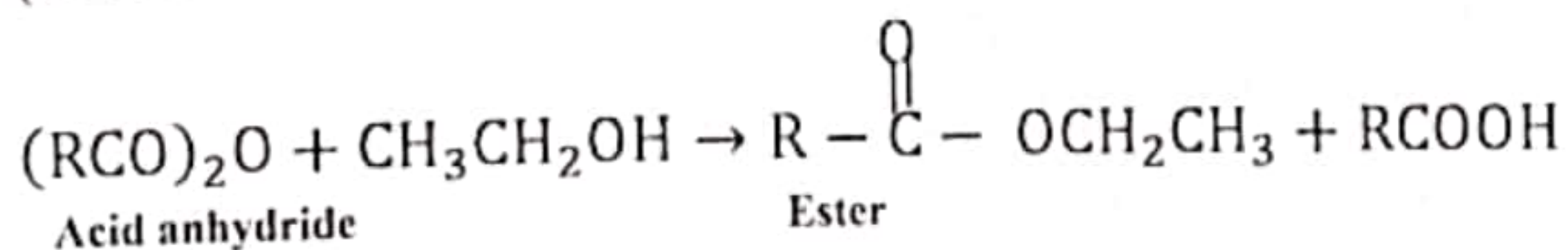
- Carboxylic acid gives positive test with ethanol under presence of strong acid catalyst by giving fruity (pleasant) smell of ester



Similarly;



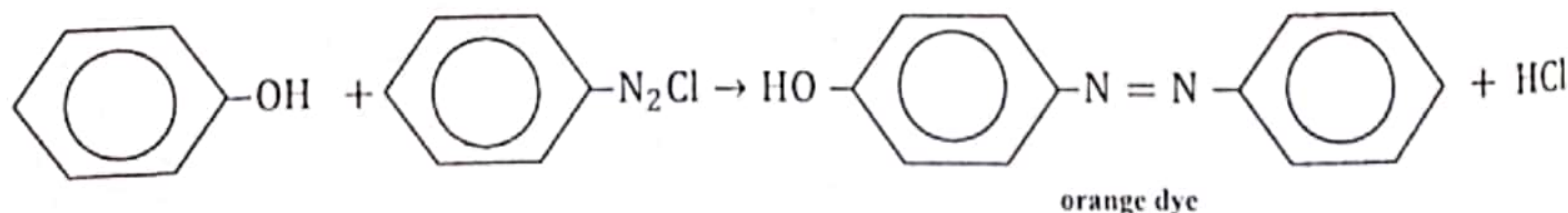
(In this case white fumes of HCl is also observed)



Dye test

This is another test of phenol. The useful reagent is benzenediazonium chloride

- Phenol reacts with benzenediazonium chloride to give an orange dye

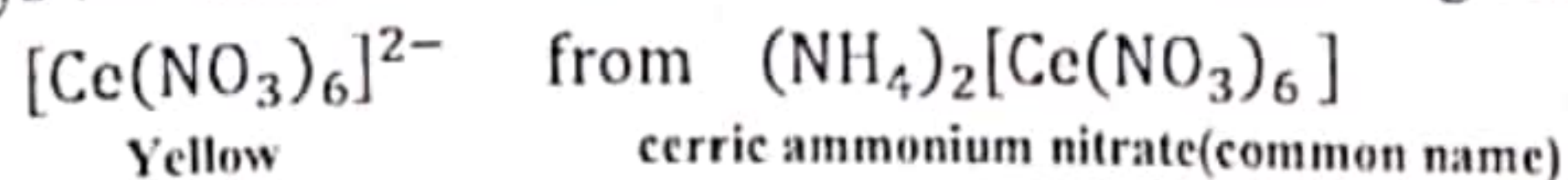


- Aliphatic alcohols not give this test.

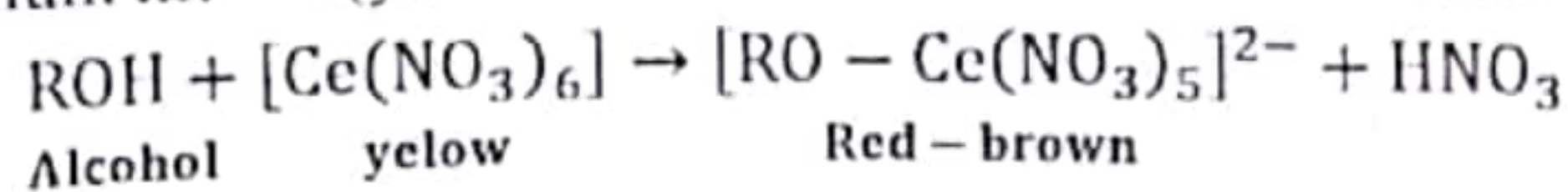
Cerrie nitrate test

This is the test of alcohols.

- It employs the cerrie nitrate complex ion with the following formula:



Alcohols give positive nitrate test by giving red-brown colouration in its reaction with cerrie ammonium nitrate (yellow colouration of cerrie ammonium nitrate disappear)



PRACTICE EXERCISE 26

Problem

Explain a chemical test to distinguish between:

- i. Trichloromethane and dichloromethane
- ii. Phenylhydrazine and 2,4-dinitrophenylhydrazine
- iii. Phenylmethanal and phenylethanal
- iv. Methyl methanoate and methyl ethanoate
- v. N-methylethanamine and N,N -dimethylethanamine
- vi. Benzene and phenol
- vii. Phenol and aniline
- viii. Aspirin and paracetamol
- ix. Dettol and common soap
- x. Phenol and benzoic acid
- xi. Ethanedioic acid and succinic acid

EXAMINATION QUESTIONS-2

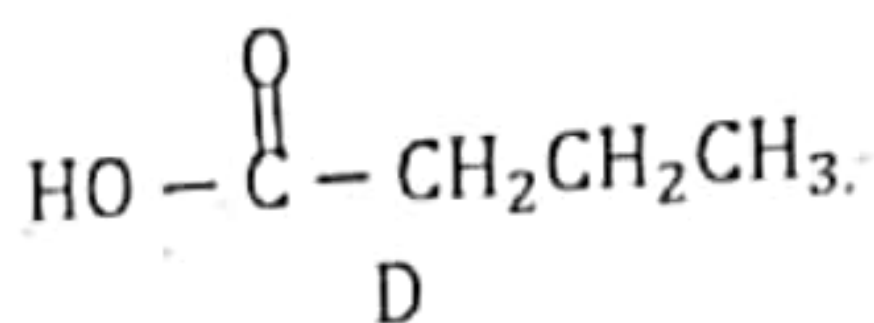
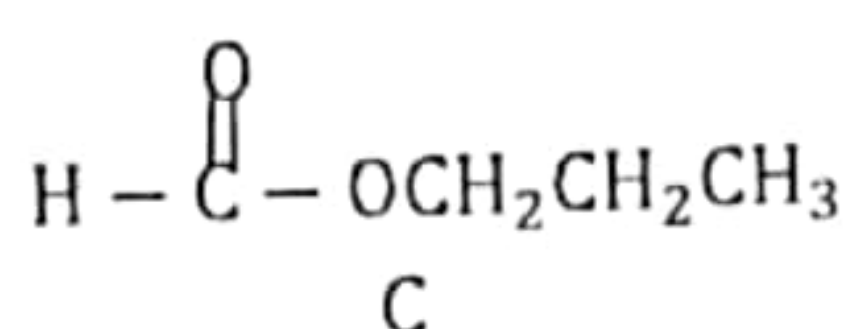
Question 1

An alcohol X has the structure $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{CH}_3)_2$

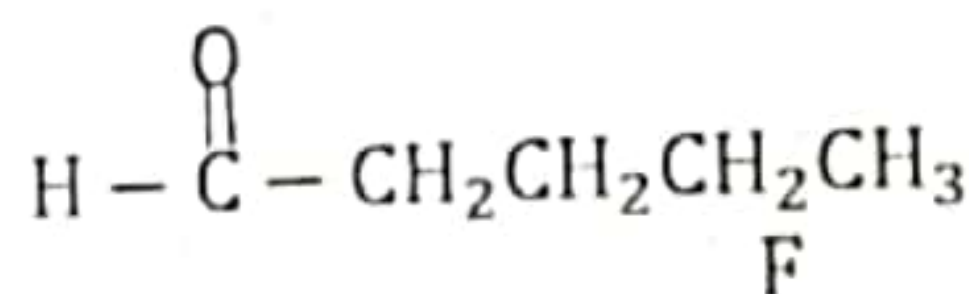
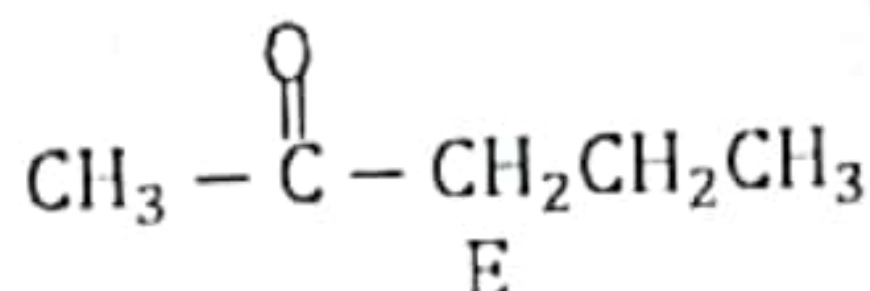
- a)
 - (i) Name alcohol X
 - (ii) Name type of reaction occurring when alcohol X is converted into 2,3- diamethylbut-2-ene in the presence of strong acid.
 - (iii) Give the structure of , and name of isomer 2,3- diamethylbut -2-ene which is also formed in the reaction . Explain why two products are obtained
- b)
 - (i) Write an equation for the reaction between alcohol X and ethanoyl chloride
 - (ii) Give an alternative method for obtaining the organic reaction product in part (b) (i), starting from alcohol X, other than using ethanoic anhydride. (State the types of reaction, the reagent(s) used and the reactions conditions).

Question 2

- a) Consider the following pair of isomers.



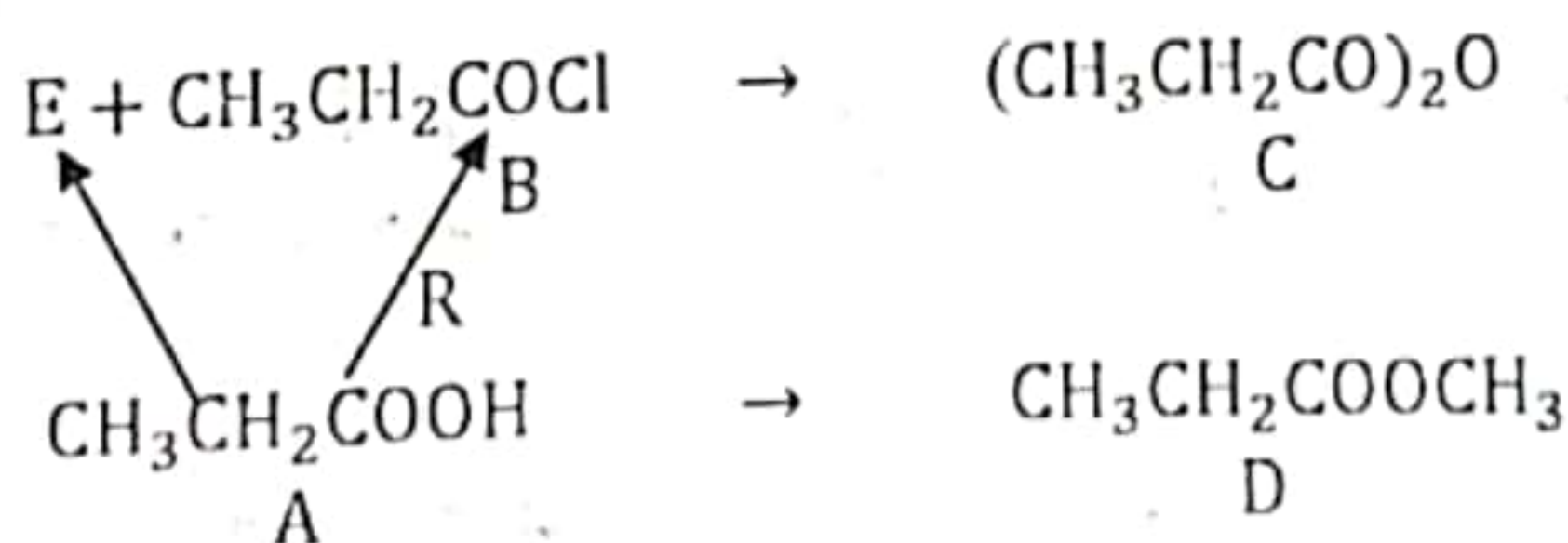
- (i) Name the compound C
 - (ii) Identify a reagent which could be used in a test-tube reaction to distinguish between C and D . In each case, state what you would observe.
- b) Consider the following pairs of isomers.



- (i) Name compound E
- (ii) Identify a reagent which could be used in a test-tube reaction to distinguish between E and F In each case, state what you would observe.

Question 3

This question is about compounds A, B, C, D and E and their inter conversions. Some of these are shown in the diagram below.



- a)
 - (i) Give the names of compounds B and C
 - (ii) Describe one observation that would be made when compound B reacts with water
 - (iii) Write an equation for the reaction that occurs when compound C is heated in water
- b) Compound A, B and C will react with the alcohol to form compound D.

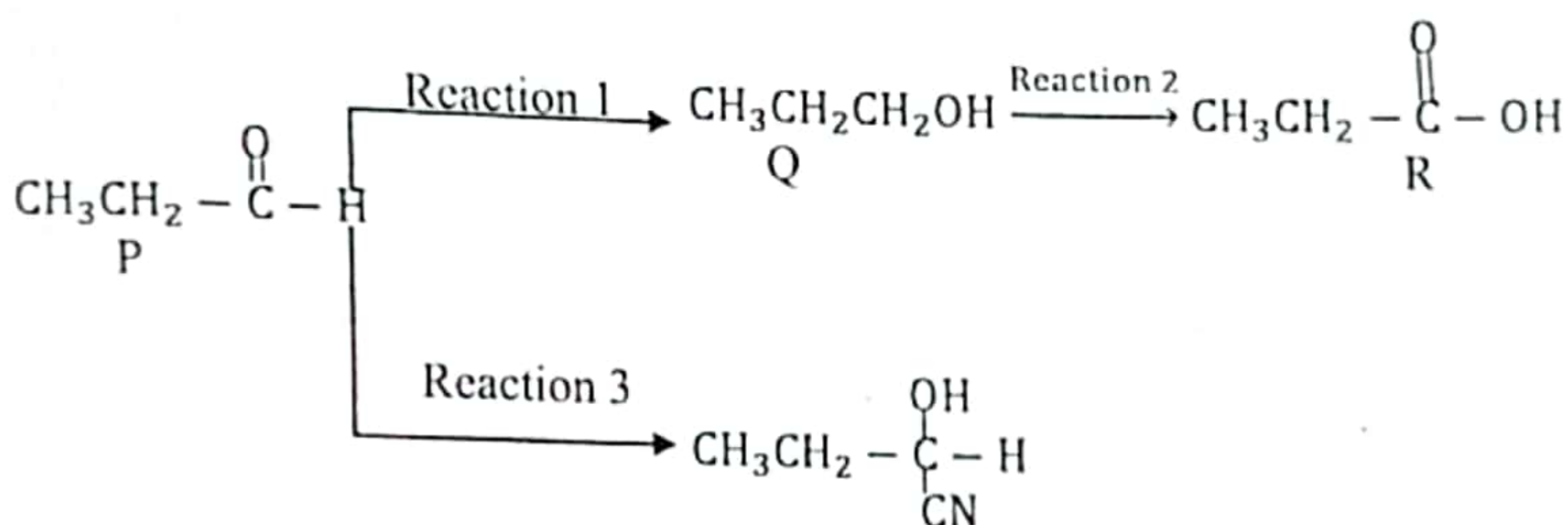
- (i) Give the name of the alcohol and the name of compound D.
- (ii) State the appropriate reaction conditions for the formation of compound D from each of the compound A, B and C.

Question 4

- a) Write an equation for the reaction of butan-2-ol with ethanoic acid, showing clearly the structure of organic product.
- b) Name the type of organic compound formed in (a) and suggest a use for this compound
- c) Give a homogeneous catalyst for the reaction in (a) and state the meaning of the term homogeneous.

Question 5

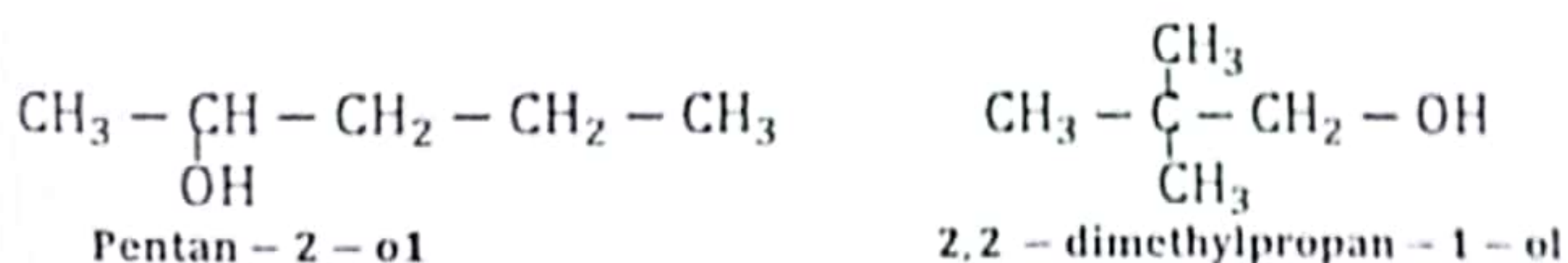
Consider the following reactions scheme.



- a) Give the reagent (s) for reaction 1 and name the type of reaction involved
- b)
 - (i) Give the reagent (s) and condition for Reaction 2
 - (ii) Write an equation for this reaction using the symbol [O] to represent the oxidizing agent.
- c) Give the reagent (s) and name the mechanism involved in Reaction 3.

Question 6

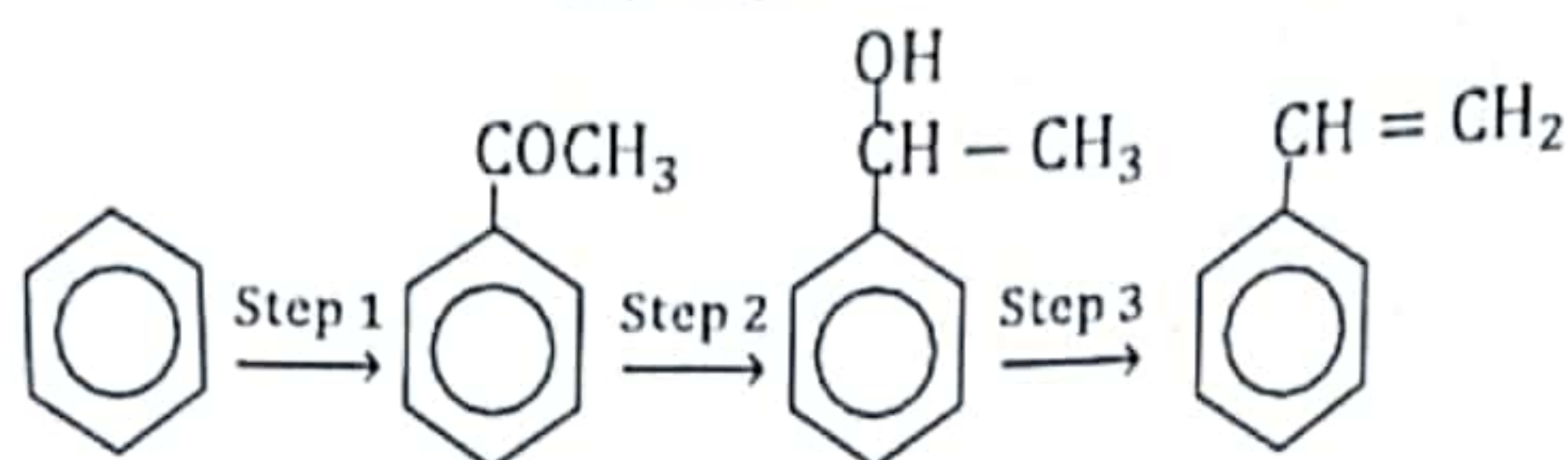
The structures of two alcohols of formula $\text{C}_5\text{H}_{11}\text{OH}$ are shown below.



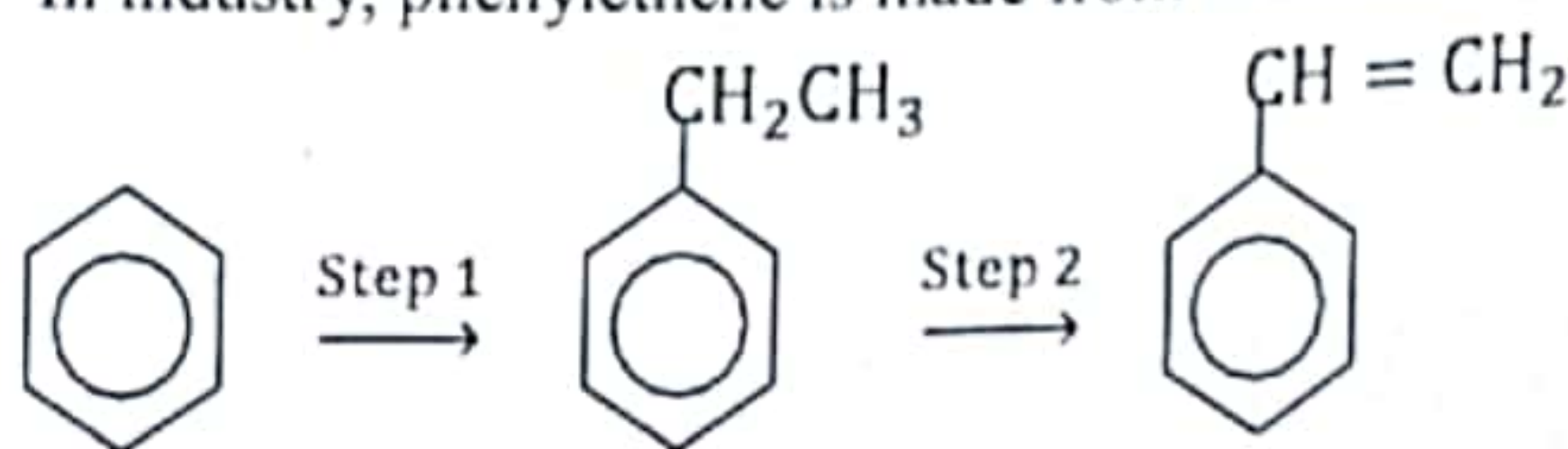
- a) A third alcohol of formula $\text{C}_5\text{H}_{11}\text{OH}$ is tertiary. Give the structure and name of this alcohol.
- b) Give the structure of major organic product when pentan-2-ol is heated with excess concentrated sulphuric acid
- c) State the type of reaction taking place in (b)
- d) Explain why the type of reaction taking place in (b) does not occur when 2, 2 dimethylpropan-1-ol is heated with the concentrated sulphuric acid.

Question 7

- a) In the laboratory, phenylethene can be obtained from benzene in a three-step synthesis.



- Give the organic reagent and inorganic catalyst used in step 1.
 - Name the type of reaction taking place in step 2.
 - Suggest either a reagent or combination of reagent and catalyst for the conversion in step 2.
 - For step 3 name the type of reaction and suggest a suitable reagent for reaction.
- b) In industry, phenylethene is made from benzene and ethane in a two-step process;



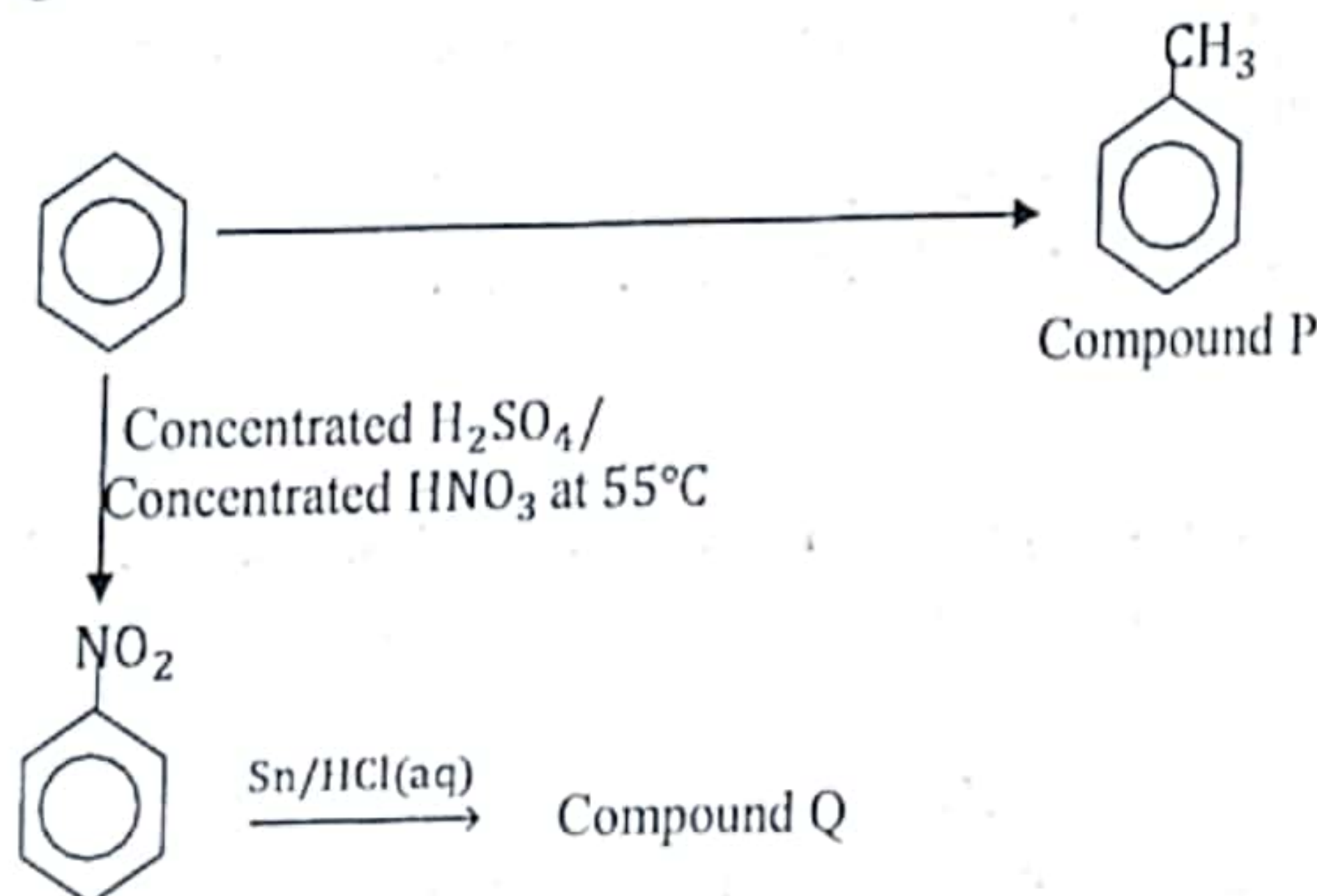
- Give one major use of phenylethene
- Identify the reactive species which attacks benzene in step 1 and write an equation to show how the species is generated.
- Name the type of reaction which occurs in step 2.

Question 8

- Write an equation for the formation of butylamine by the reaction of ammonia with 1-bromobutane.
- Butylamine can also be prepared in two step synthesis starting from 1-bromopropane. Write an equation for each of the two steps in this synthesis.
- Explain why butylamine is a stronger base than ammonia
 - Identify a substance that could be added to aqueous butylamine to produce a basic buffer solution.

Question 9

The figure shows a reaction scheme for some aromatic compounds

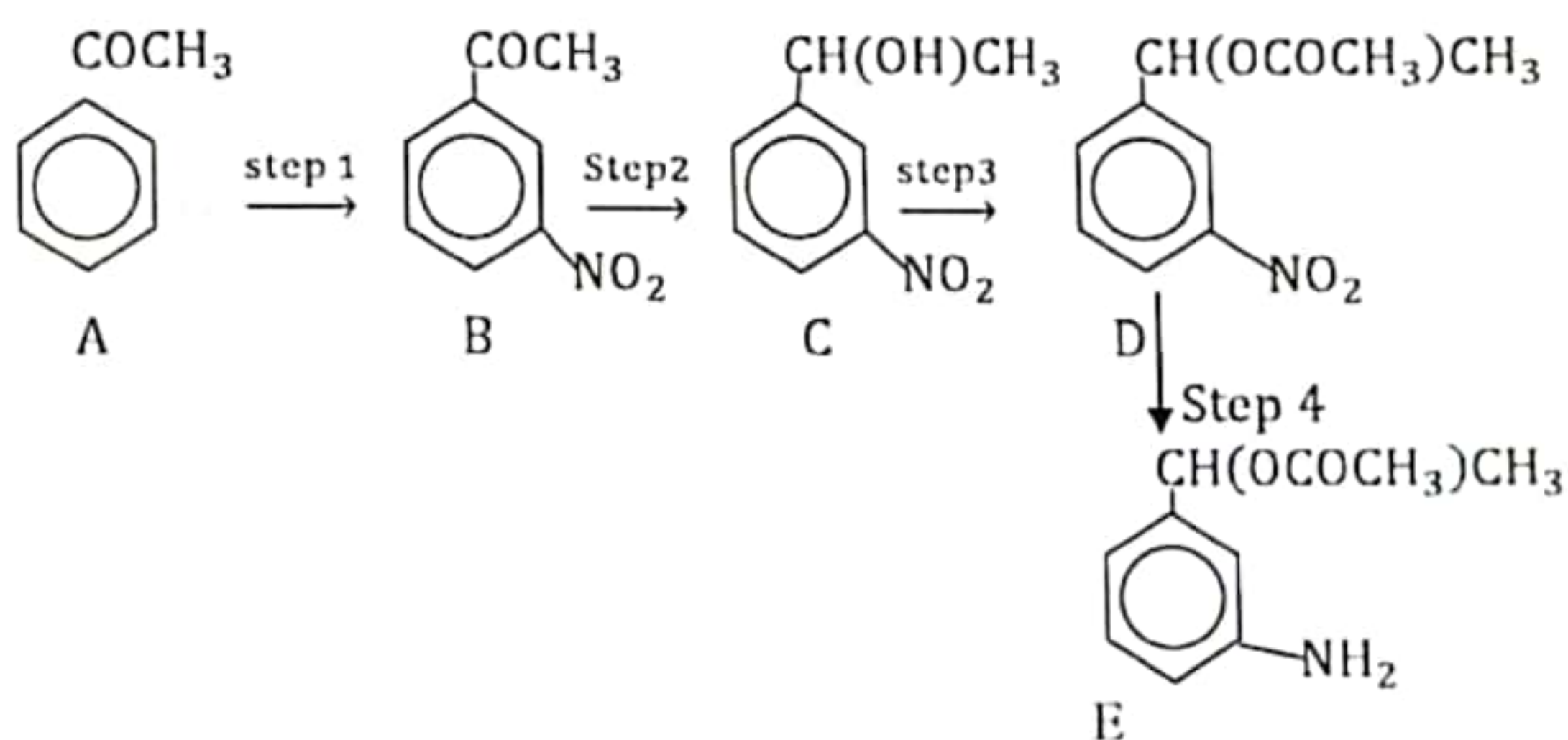


- Give the reagents and conditions for the conversion of benzene into compound P.

- (ii) Give the name of the mechanism of this reaction
- b) Write structure of possible organic products when excess chlorine is passed through boiling point compound P in strong sunlight
- c)
- Classify the type of reaction occurring when nitrobenzene is converted to compound Q
 - Give a structure of compound Q
- d) Classify the type of reaction and give the structure of the organic products of the reaction of propanal with ;
- Sodium tetrahydridoborate (III)
 - Fehling's solution
 - Hydrogen cyanide

Question 10

Consider the following reaction sequence.



- a)
- Give the reagents required to carry out step 1 and write an equation for the formation of the inorganic reactive intermediate involved.
 - Name and outline the mechanism for the reaction between this intermediate and compound A.
- b) Name the type of reaction taking place in step 2 and suggest a suitable reagent or combination of reagents for this conversion.
- c) Suggest derivative of ethanoic acid which could be used as a reagent for carrying out step 3.
- d) Name the type of reaction taking place in step 4 and suggest a suitable reagent or combination of reagents for this conversion.

Question 11

(Phenylmethyl)amine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, can be prepared from (bromomethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ and also from benzenecarbonitrile, $\text{C}_6\text{H}_5\text{CN}$.

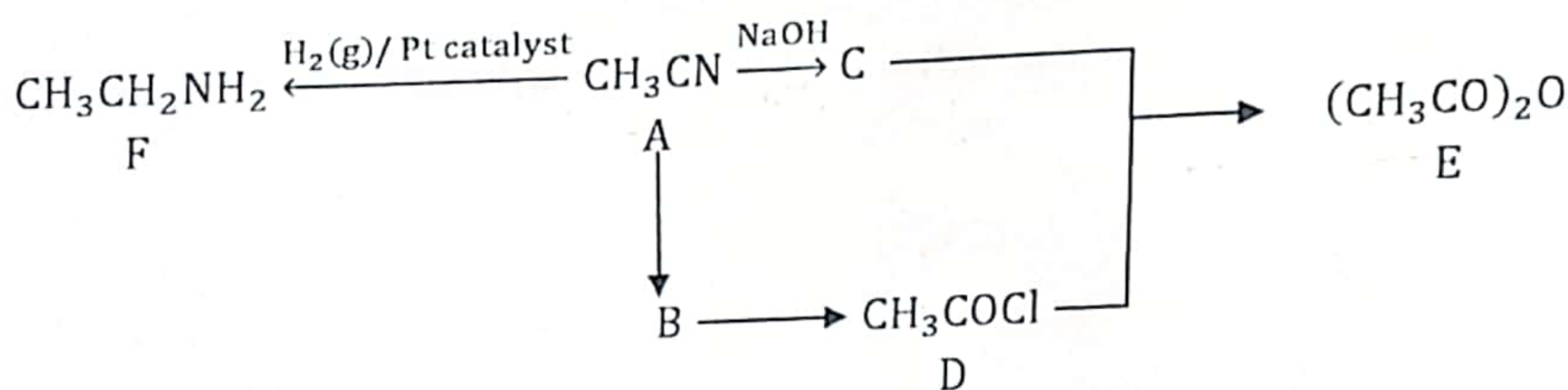
- a)
- Write an equation for the conversion of (bromomethyl)benzene into (phenylmethyl)amine. Name the type of reaction taking place and explain why a low yield of product is obtained.

Ngaiza's series of advanced chemistry

- (ii) Name the type of reaction involved in the conversion of benzenecarbonitrile into (phenylmethyl)amine. Write an equation for this reaction and suggest a suitable reagent or a combination of reagent and catalyst. Explain why this method of preparation gives a high yield of product
- b) State which of the two amines, (phenylmethyl)amine and phenylamine, $C_6H_5NH_2$, is the weaker base, and explain your choice.

Question 12

Consider the following reaction scheme and answer the questions below.



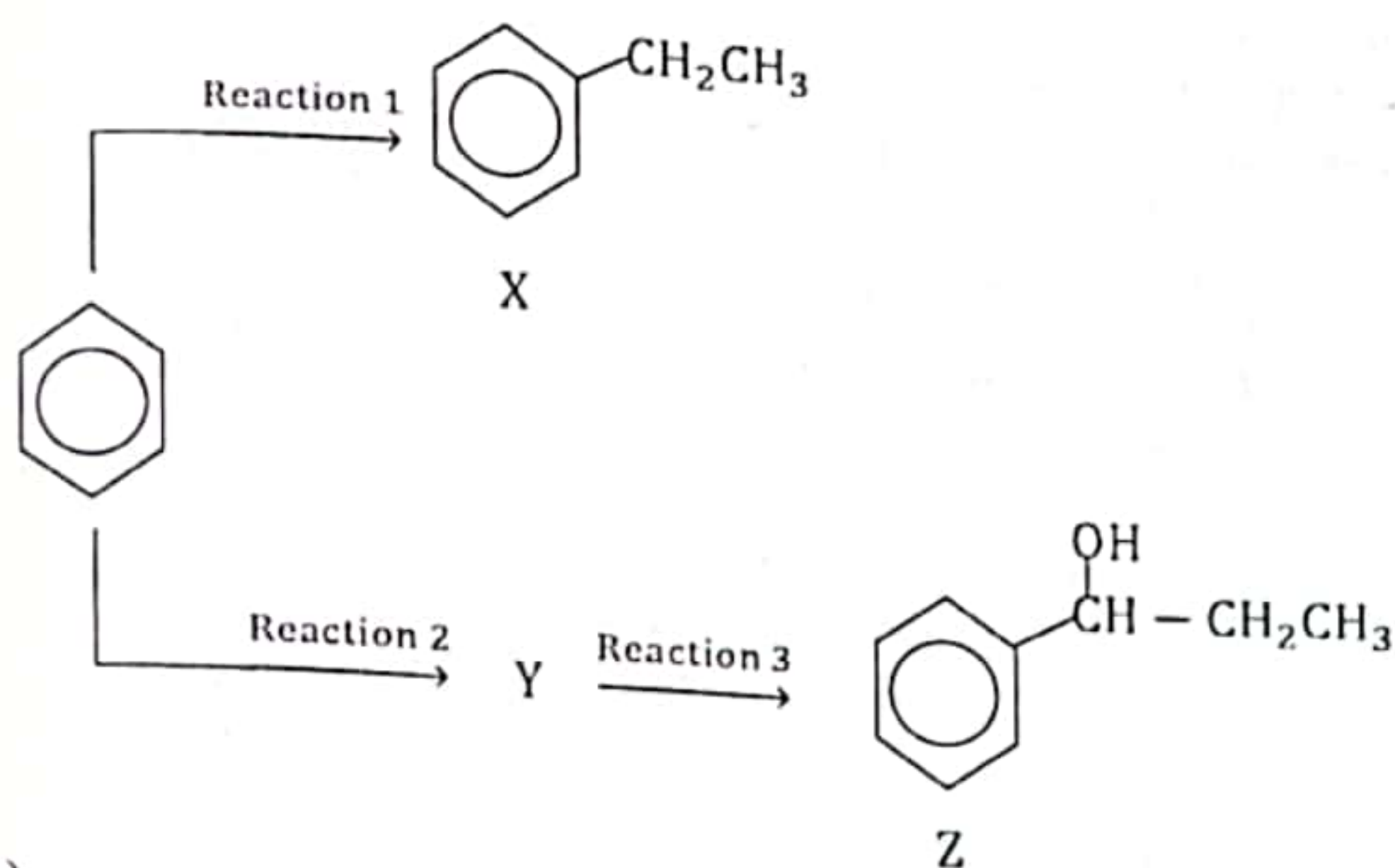
- a) The reaction of compound C With D produce compound E
- Give the structure of E
 - State the compound type to which E belongs.
- b) Compound F may be prepared by the reaction of A with hydrogen gas in the presence of platinum catalyst.
- Give the name of F
 - Suggest the type of reaction involved in the conversion of A into F
- c) Compound D and F react readily together. Write an equation for the reaction between them.

Question 13

- a)
- Write an equation for the reaction between propanoyl chloride and methylamine.
 - What is the type of the chemical reaction in a (i) above?
- b) Benzene reacts with propanoyl chloride the presence of aluminum chloride. Write an equation to show the role of aluminum chloride as a catalyst in this reaction and write the structure of organic product formed in the reaction.
- c) Write an equation for the reaction of propanoyl chloride with water. An excess of water is added to 1.48g of propanoyl chloride. Aqueous sodium hydroxide is then added from a burette to the resulting solution. Calculate the volume of 0.42 mol dm^{-3} aqueous sodium hydroxide needed to react exactly with the mixture formed.

Question 14

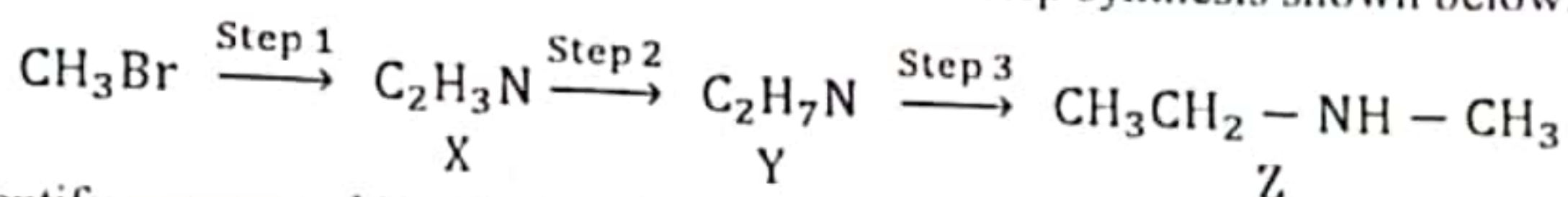
Two reactions of benzene are shown below



- a)
- Name X and give the reagent and catalyst of the required for reaction 1.
 - Write an equation for the formation of the reactive intermediate involved in this reaction.
- b)
- Deduce the structure of Y and give the organic reagent needed for reaction 2
 - Give the reagent(s) needed for reaction 3

Question 15

Compound Z can be formed via compound X and Y in three step synthesis shown below.



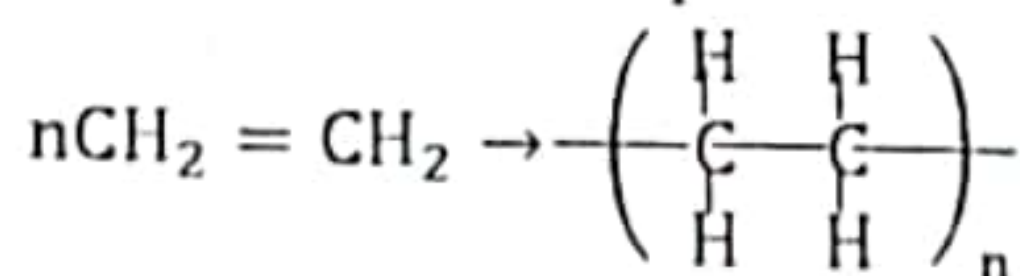
- Identify compound X and Y and give reagents and conditions for step 1 and 2
- State the type of compound of which Z is an example.
- Compound Z reacts with a large excess bromoethane to form a solid product. Draw the structure of this product and mention at least two uses of it.

Question 16

- Write an equation for the reaction between ethanoyl chloride and ethanol
- Explain why dilute sodium hydroxide will cause holes to appear in clothing made from polymers such as Terylene but a poly (phenylethene) container can be used to store sodium hydroxide.

Question 17

- Classify the following reaction $\text{C}_3\text{H}_7\text{Br} + \text{KOH} \rightarrow \text{C}_3\text{H}_6 + \text{KBr} + \text{H}_2\text{O}$
- How do physical properties of the alkene homologous series change as the chain length increases?
- For the reaction shown in the equation



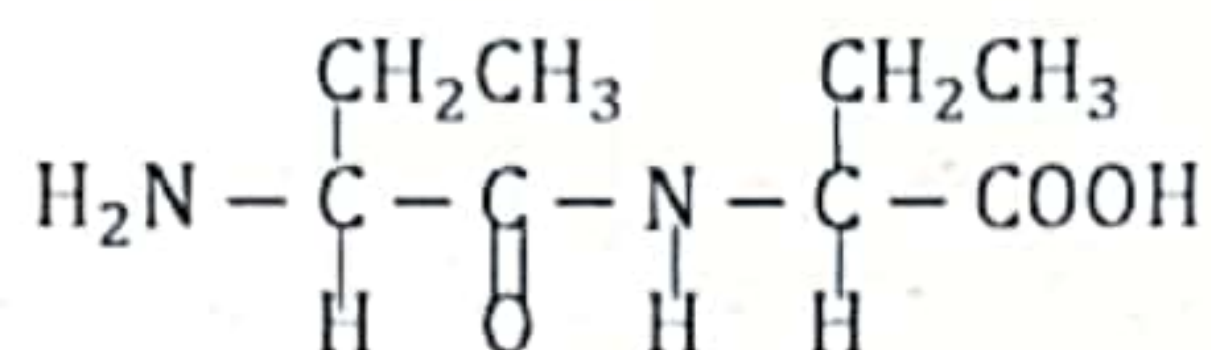
Give the name of this process

d) Most ethanol used in the chemical industry is manufactured by reacting together water and ethene

- (i) Write a balanced equation for this reaction
- (ii) Outline the reaction conditions for this reaction(In industries)
- (iii) Classify this reaction, indicating the type of initial attack on the ethene

Question 18

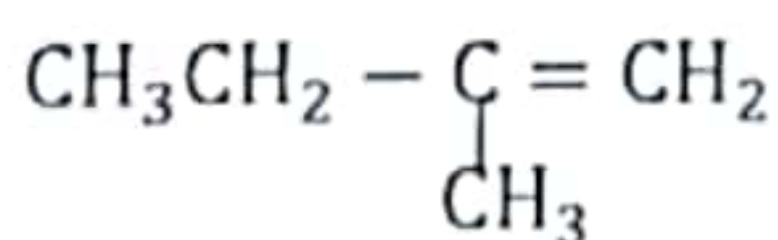
- a) The compound $\text{H}_2\text{C} = \text{CHCN}$ is used in the formation of acrylic polymers
- (i) Draw the repeating unit of the polymer formed from this compound
 - (ii) Name the type of polymerisation involved in the formation of this polymer
- b) When the dipeptide shown below is heated under acidic conditions a single amino acid is produced



- i) Name this amino acid
 - ii) Draw the structure of the amino acid species present in the acidic solution
- c) The repeating unit of polyester is shown below
- $$\left[\text{CH}_2\text{CH}_2 - \text{O} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{CH}_2\text{CH}_2 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{O} \right]$$
- (i) Deduce the empirical formula of the repeating unit of this polyester
 - (ii) Draw the structure of the acid which could be used in the preparation of this polyester and give the name of this acid.
 - (iii) Give one reason why polyester is biodegradable

Question 19

- a) The hydrocarbon M has the structure shown below;



- (i) Name the hydrocarbon M
 - (ii) Draw the repeating unit of the polymer which can be formed from M. State the type of polymerisation occurring in this reaction
 - (iii) Draw the structure of the major product formed in the reaction between M and benzene in presence of HCl and AlCl_3
 - (iv) Draw a structural isomer of M which shows geometric isomerism
- b)
- (i) Draw the repeating unit of the polymer formed by the reaction between butanedioic acid and hexane - 1,6 - diamine
 - (ii) State type of polymerisation occurring in b(i) above and give a name for the linkage between monomers units in this polymer

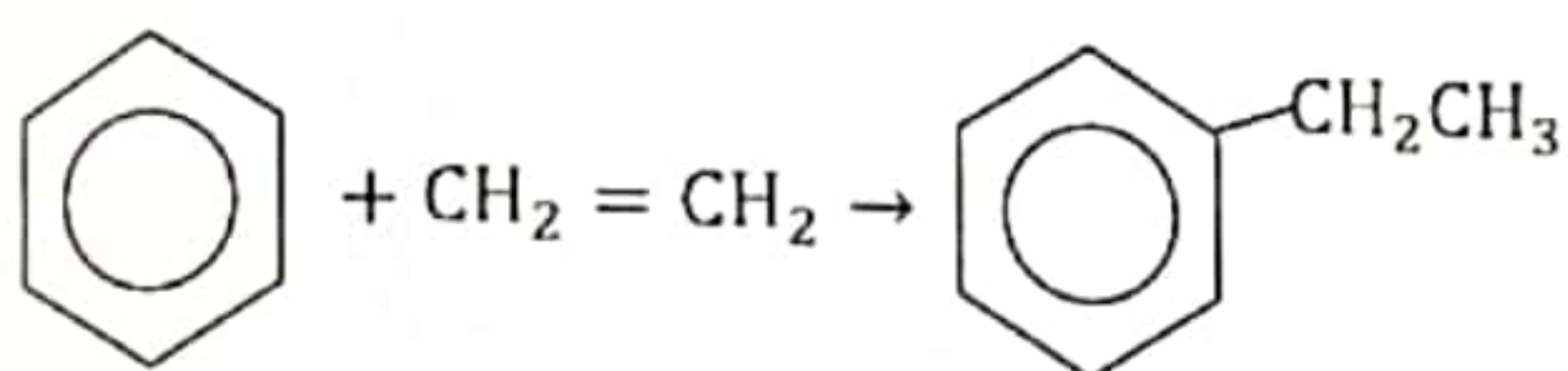
Question 20

- a) "Terylene" is a condensation polymer that can be formed from benzene -1,4-decarboxylic acid and ethane - 1,2 - diol. Draw the structure of;
- (i) Benzene - 1,4 dicarboxylic acid
 - (ii) Ethane - 1,2 - diol

- (iii) The polymer "Terylene"
- b) Give the name of the type of condensation polymer of which "Terylene" is an example
- c) Outline the difference between the formation of addition polymer and a condensation polymer
- d) Give the name of one addition polymer

Question 21

Ethylbenzene is made by the reaction shown below:



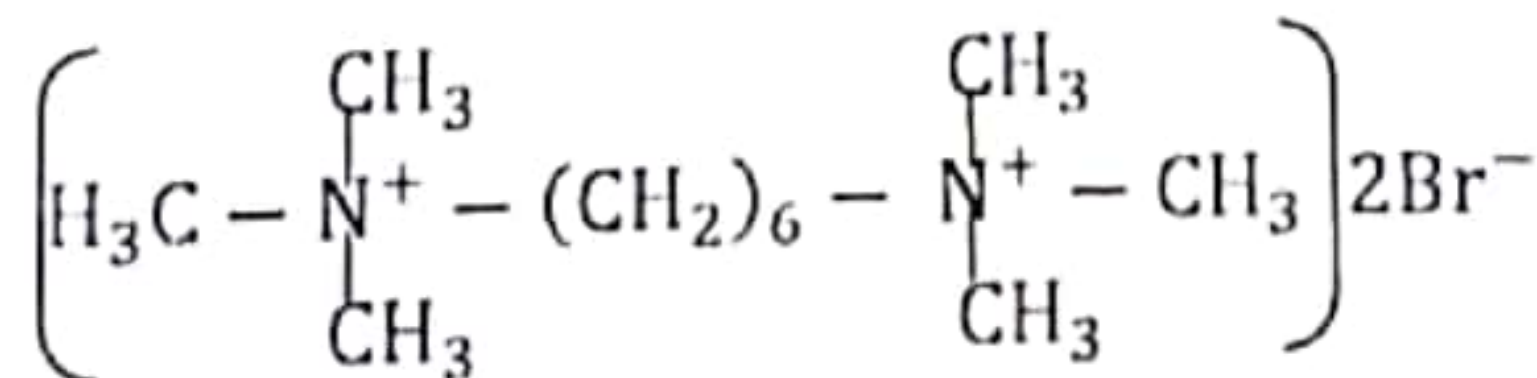
- a)
 - (i) Identify two other substances required as catalysts in this preparation
 - (ii) Give equations to reflect the role of each substance mentioned in (a) (i) above and hence write the overall equation for the reaction of these two substances with ethene to form the reactive intermediate involved, in the formation of ethylbenzene.
- b) Draw the structure of the product formed in a similar reaction between benzene and cyclohexene.



- c) Ethylbenzene is used to make phenylethene which can be polymerised to form poly (phenylethene). Name this type of polymerisation and draw the structure of the repeating unit in the polymer.

Question 22

- a) Synthetic polyamides are produced by the reaction of dicarboxylic acids with compounds such as $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
 - i) Name the compound $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
 - ii) Give the repeating unit in the polyamide nylon-6,6.
- b) Synthetic polyamides have structures similar to those found in proteins.
 - i) Draw the structure of 2 – aminopropanoic acid
 - ii) Draw the structure of product formed by the condensation of two molecules of 2 – aminopropanoic acid
- c) Compounds like $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ are also used to make ionic compound such as X shown below.

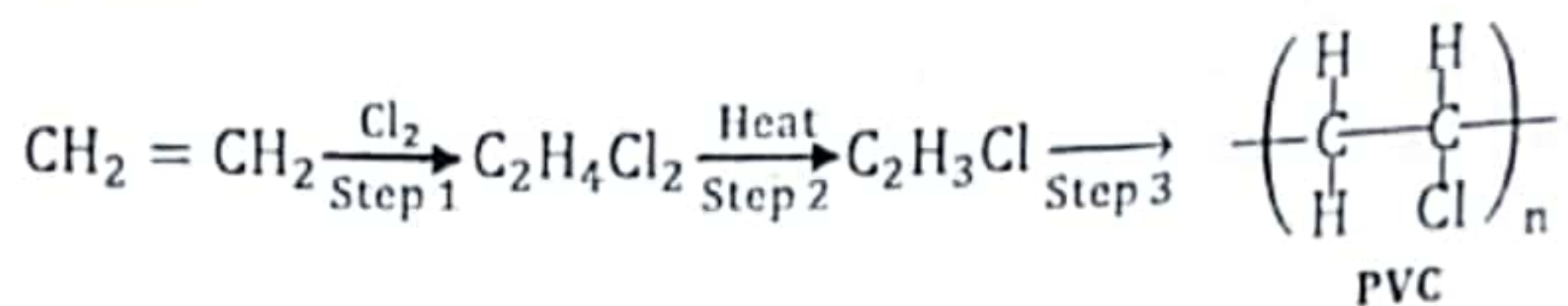


Compound X

- i) X belongs to the same type of compound as $(\text{CH}_3)_4\text{N}^+\text{Br}^-$. Name this type of compound
- ii) State the reagent which would produce X from $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ and give a necessary condition to ensure that X is the major product
- iii) Name the type of reaction involved in the formation of X

Question 23

The polymer poly (chloroethane), commonly known as poly (vinylchloride) or PVC, can be produced as follows:



- Write an equation of step 2 showing clearly the structure of organic product
- Plasticizers are often incorporated into polymers such as PVC. Name a type of compound used as a plasticizer.
- Draw the structure of the organic product of the reaction $\text{C}_2\text{H}_4\text{Cl}_2$ with an excess of warm aqueous sodium hydroxide.
 - Suggest why $\text{C}_2\text{H}_3\text{Cl}$, the organic product of step 2, does not react with warm sodium hydroxide

Question 24

This question concern the chemistry of ethene and compounds derived from it consider the following statements and then answer the question below.

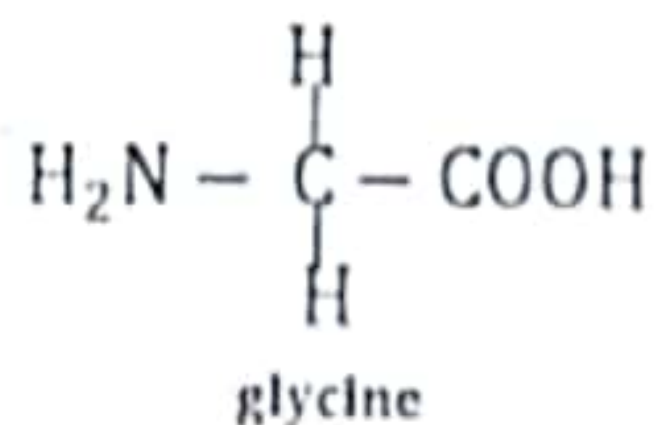
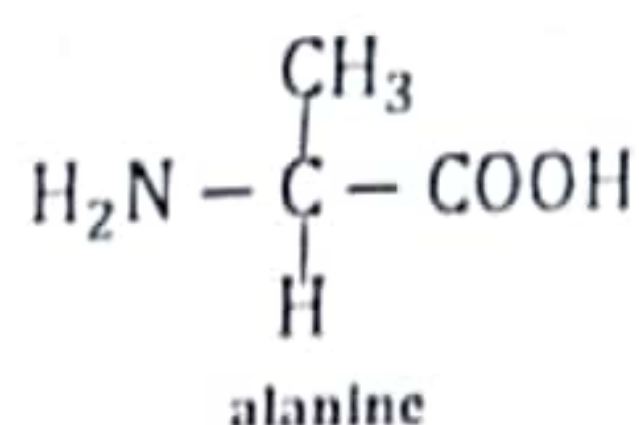
- Ethene may be polymerised to form poly(ethene)
- Treatment of ethene with bromine gives a compound C.
- Compound C may be converted in the laboratory into compound D, which has a percentage composition by mass of ; C 38.71%, H 9.68%; O 51.61%

The relative molecular mass, M_r of D is 62.

- Explain what is meant by the term polymerisation
 - Write an equation to represent the polymerisation of ethane
- Give the name of compound C
- What is the type of reaction between ethene and bromine and write the equation for the reaction
- Use the analytical data provided at the start of question to deduce the molecular formula of compound D.
 - Give the reagent(s) and condition(s) for the conversion of C into D
 - Write an equation for the conversion C into D

Question 25

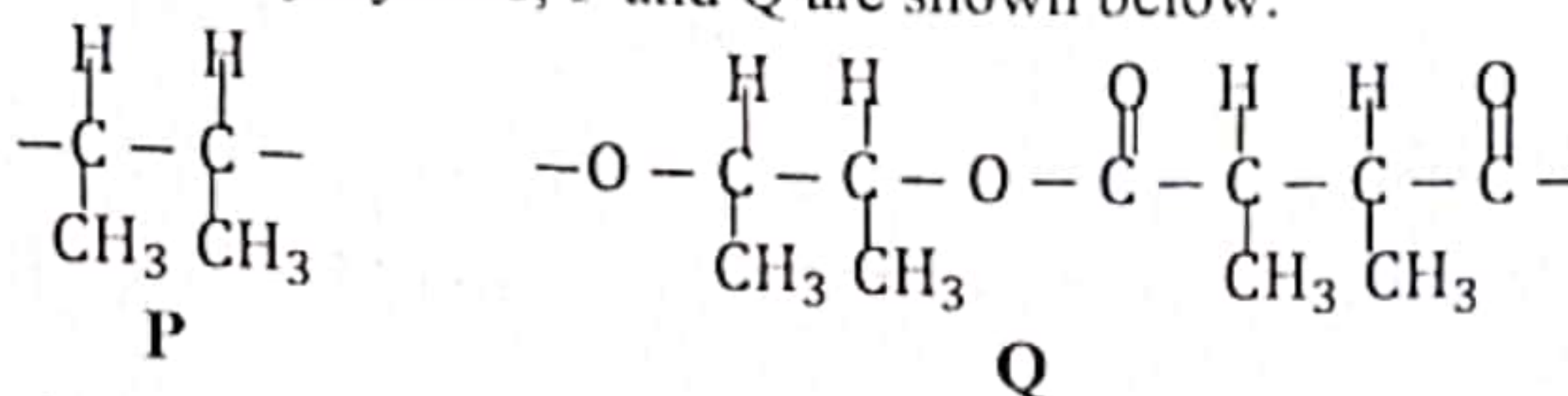
The structures of the amino acids, alanine and glycine are shown below.



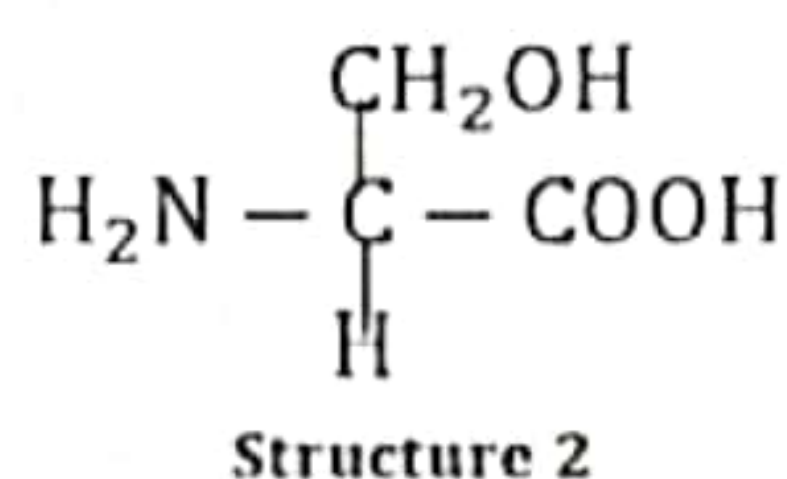
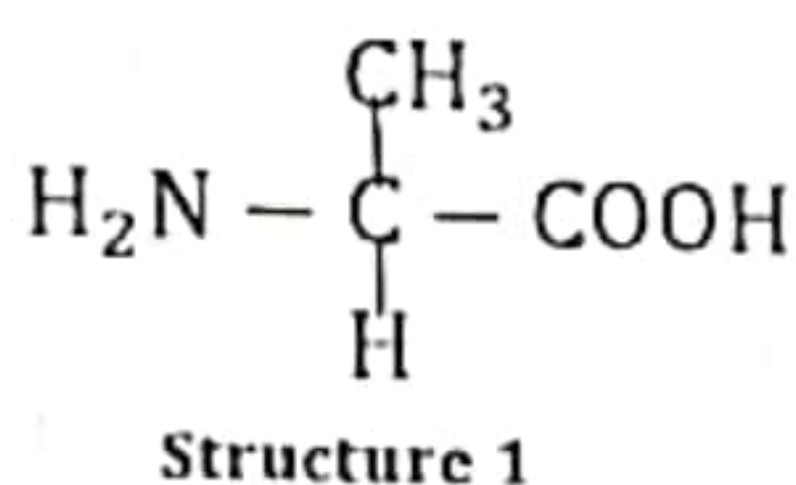
- Give systematic name for alanine and glycine
- Give the formula of the species formed by glycine at (i) pH 14 (ii) pH 2.
- When two amino acids react together, a dipeptide is formed Give the structural formulae of the two dipeptides which are formed when alanine and glycine react together
- Give the structural formula of the organic compound formed when glycine reacts with methanol in the presence of a small amount of concentrated sulphuric acid.

Question 26

- a) The repeating unit of two polymers, P and Q are shown below.

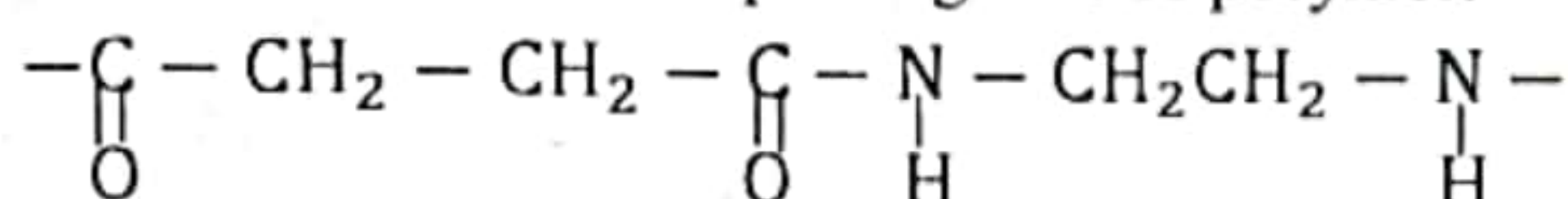


- Draw the structure of the monomer used to form polymer P. Name the types of polymerisation involved.
 - Draw structures of two compounds which react together to form polymer Q. Name these two compounds and name type of polymerisation involved.
 - Identify a compound which in aqueous solution will break down polymer Q but not polymer P.
- b) Draw the structure of the dipeptides which can form when one of the amino acids shown below reacts with the other.



Question 27

- a) The structure below shows the repeating unit of polymer.

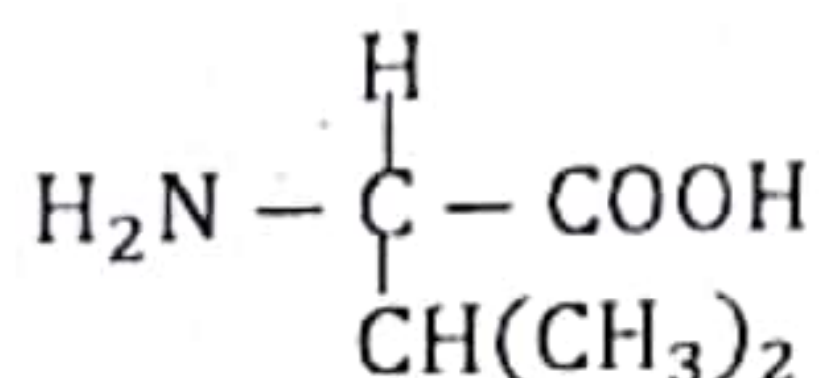


By considering the function group formed during polymerisation, Name this type of polymer and the type polymerisation involved in its formation.

- Draw the structure of the species present in solid aminoethanoic acid, $\text{H}_2\text{NCH}_2\text{COOH}$
- Explain why the melting point of aminoethanoic acid is much higher than that of hydroxybenzoic acid HOCH_2COOH .

Question 28

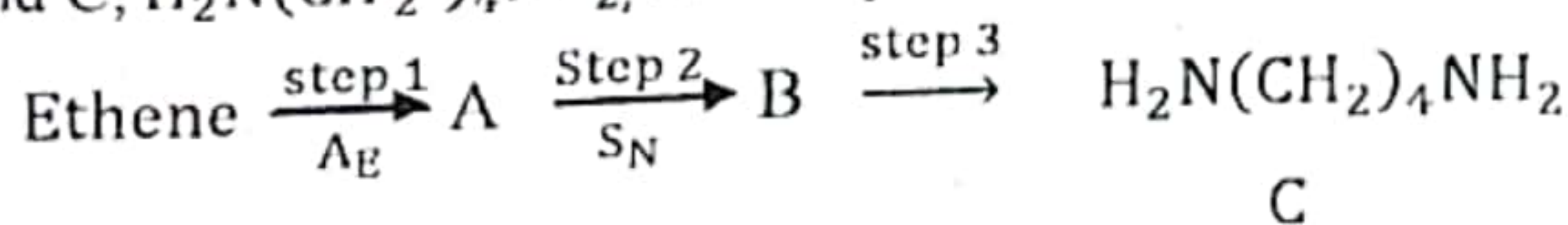
Consider the following amino acid.



- Draw the structure of the amino acid species present in a solution at pH 12
- Draw the structure of the dipeptide formed from two molecules of this amino acid
- Protein chains are often arranged in the shape of helix. Name the type of interaction that is responsible for holding the protein chain in this shape

Question 29

- a) Compound C, $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$, can be synthesized from ethane in three steps as shown below.



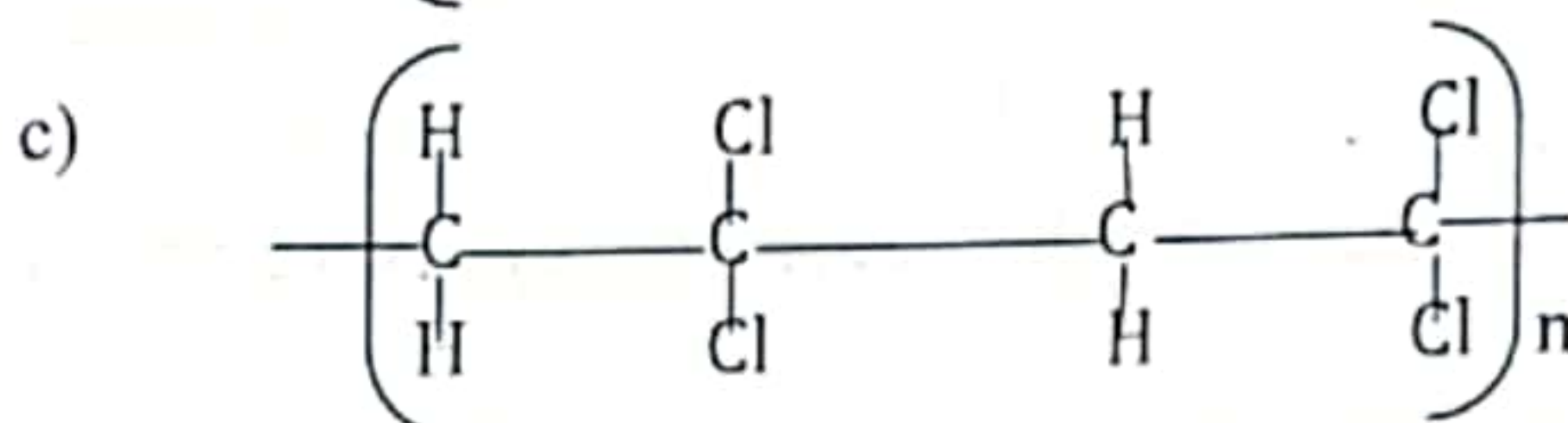
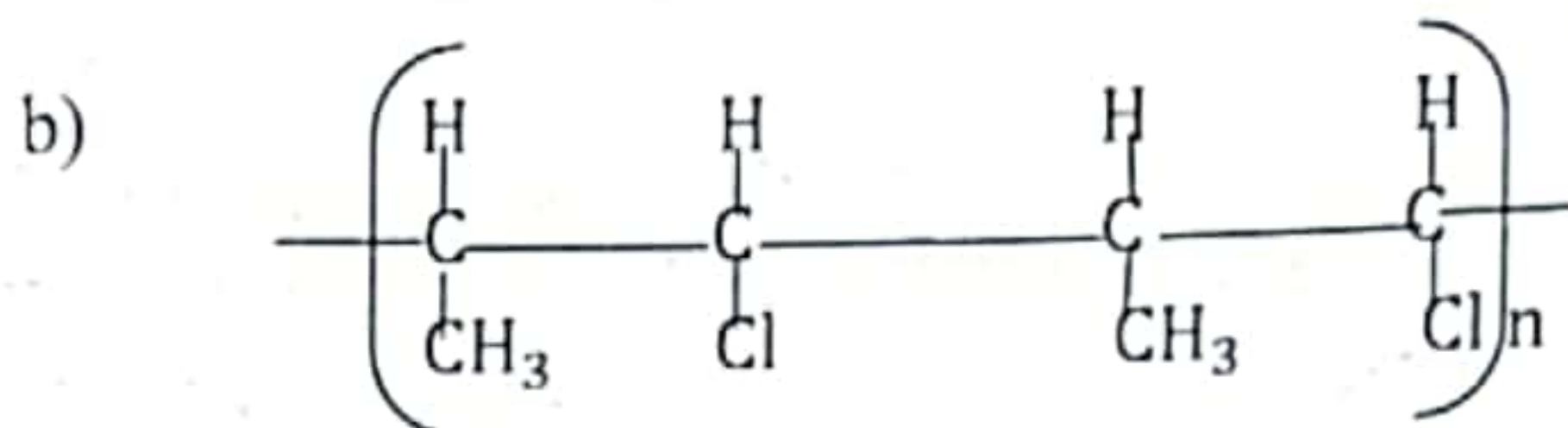
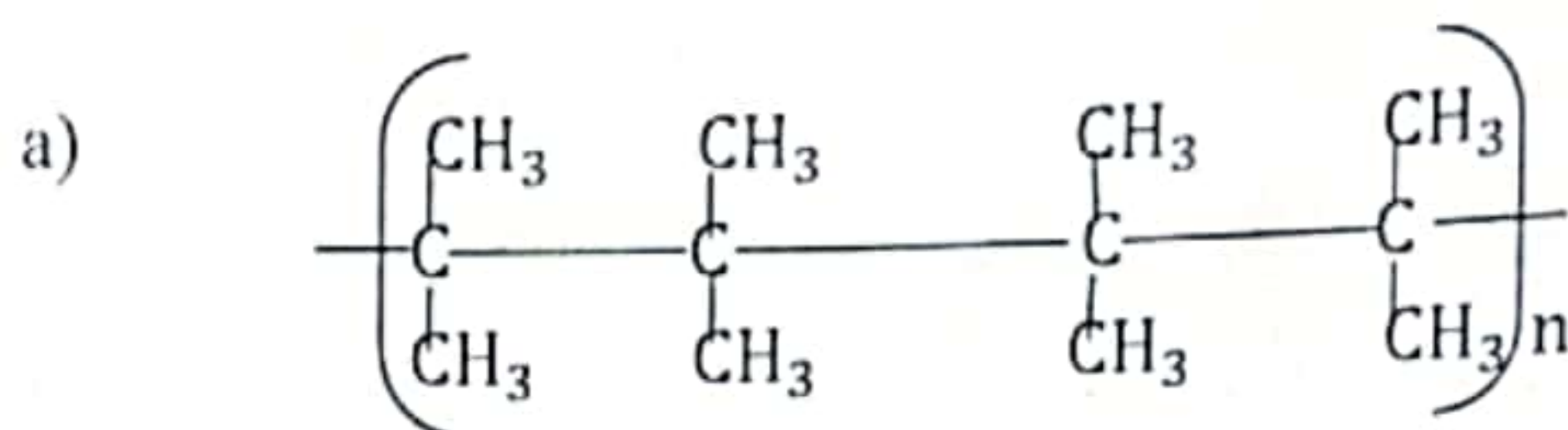
Name compound C and draw a structure for each A and B. State the reagent(s) required for each step and name the type of reaction involved in the conversion of B into C.

- b) Draw the repeating unit of the polyamide formed when C reacts with hexanedioic acid and state type of the interactions between the chains of the polyamides.

Question 30

For each of the following polymer;

- Draw the monomer from which the polymer is made.
- Name the polymer



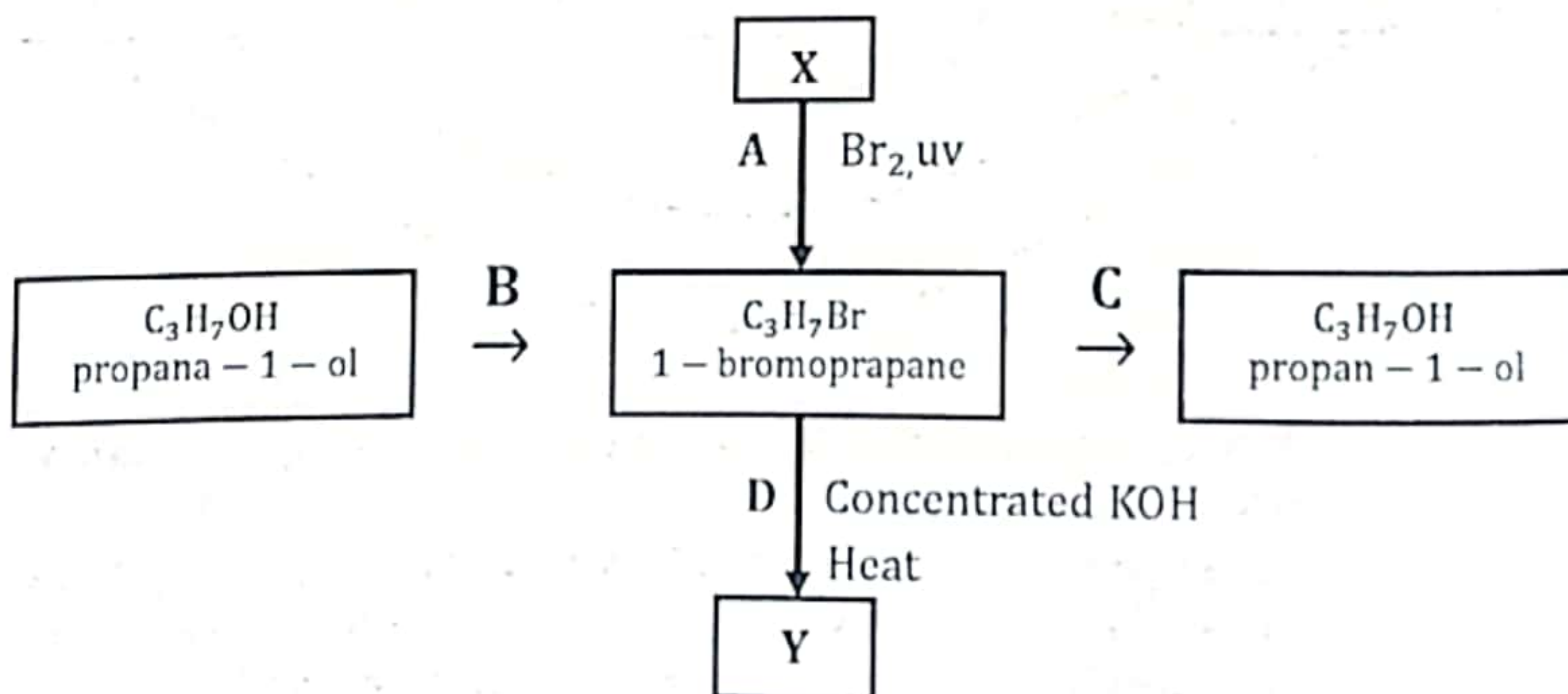
Question 31

Predict the products of the following reactions

- Benzene – 1,4 – dicarboxylic acid with 1,2 – diaminoethane
- Hexane – 1,6 – diol chloride with propane – 1,2 – diol
- Ethanedioic acid with ethane – 1,2 – diol

Question 32

Some organic reactions are shown in the flow diagram below



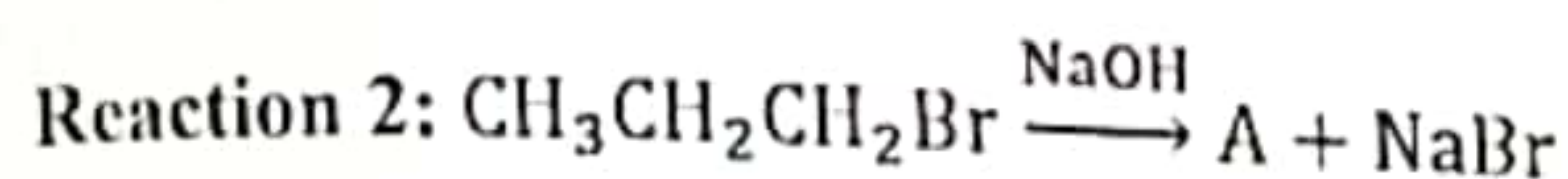
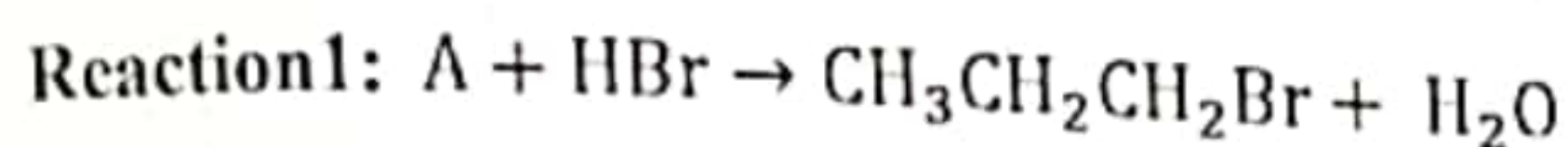
- Name the type of reactions illustrated by A, B, C and D
- Use condensed structural formulae and write a balanced equation for reaction C
- Write down structural formula of compound X
- In order to obtain product Y, $\text{C}_3\text{H}_7\text{Br}$ is heated with concentrated solution of KOH under reflux. Use condensed structural formulae to write a balanced equation for the reaction.

- e) Group learners decided to heat C_3H_7Br with dilute sodium hydroxide instead of concentrated potassium hydroxide under reflux.

Write down IUPAC name of the organic compound that they will obtain.

Question 33

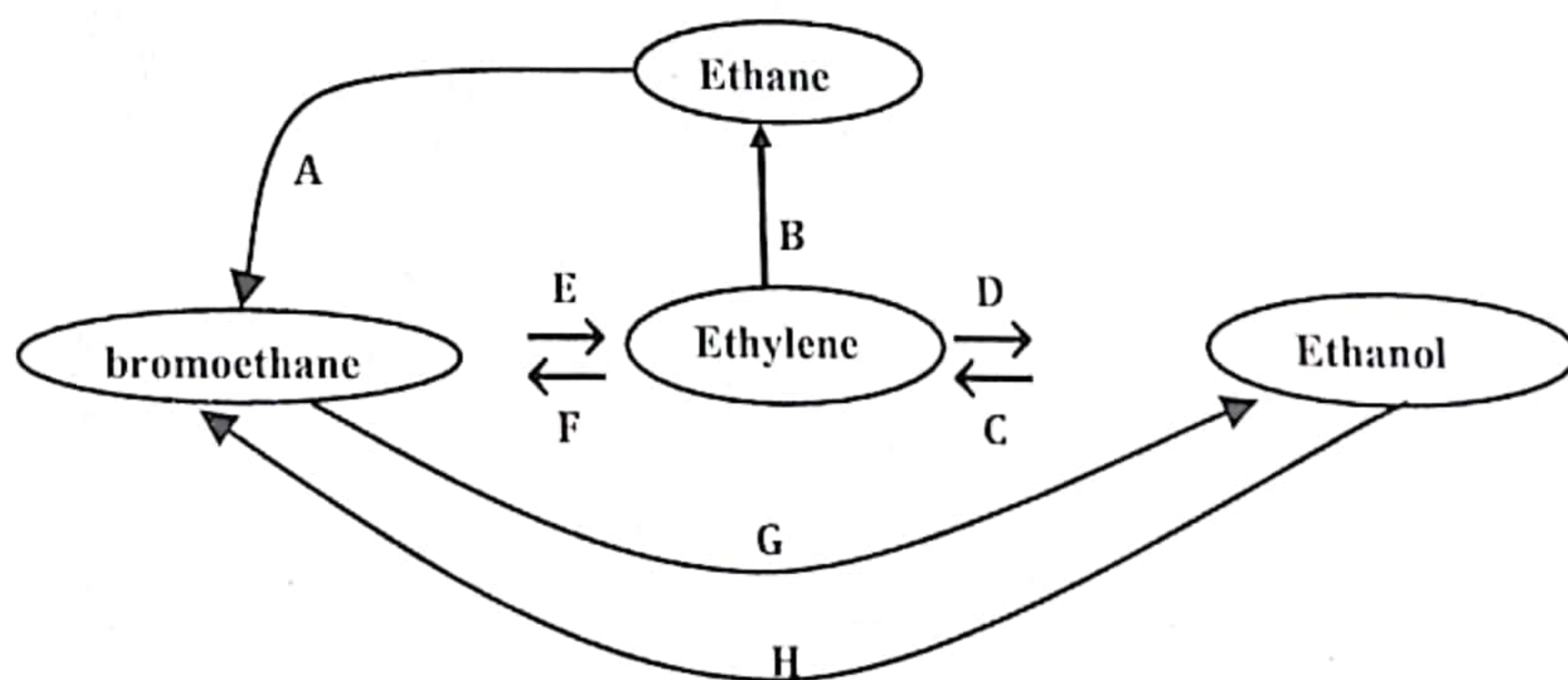
The following equation represents chemical reaction;



- Name the type of reaction in reaction 2
- Write down the structure of the organic compound A

Question 34

- Ethylene is gaseous hormone associated with the ripening of fruit. It also contributes to the ageing and distortion of plants in industry. The artificial ripening of fruit takes place where ethylene is passed over the fruit in large rooms, after a while the ripening fruit releases its own ethylene.
 - Write down the structure of ethylene
 - Why is not advisable to place banana that has been artificially ripened alongside a cabbage.
- In industry, ethylene is also used to synthesis a variety of organic compounds, the flow diagram illustrates some of the many reactions of ethylene undergoes.



- Write down the general molecular formula for the homologous series to which ethylene belongs.
 - Name type of reactions represented by each of letters A, B, C, D, E, F, G and H
 - Use structure formulae to write down a balanced equation for reaction B.
 - Apart from ethylene, which other reactant is needed for reaction F?
- c) Both reactions E and G (in (b) above) occur in presence of a base.
- How the base in reaction E is different from the base in reaction G?
 - Name the type of elimination reaction represented by E.

Question 35

More than 90 million organic compounds are known to man today. In the table below the letter A to E represent a few of these compounds

	COMPOUND
A	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
B	Trimethylamine
C	$\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_3$
D	6 - Methyl - 1 - heptene
E	$\text{CH}_3\text{CONHCH}_3$

- Write down IUPAC name of compound C
- Write down structural formula of compound D
- To which homologous series does compound E belongs?
- Write down the IUPAC name of function isomer of A
- Compound B is one of the substances responsible for the fish odour (smell) of fish Explain why serving lemon slices with fish reduces the odour.

Question 36

There are two structural isomers for the organic compound with molecular formula $\text{C}_2\text{H}_4\text{O}_2$

- Define the term structural isomers:
- Write down the structural formula of these two isomers and hence give their names
- State with reasons, which one of these isomers
 - Has higher boiling point.
 - Has higher vapour pressure.

Question 37

Rubber is a naturally occurring compound. The diene, 2 - methyl - 1,3 - butadiene, is one of the repeating units found in rubber. Over 20 million families depend on rubber cultivation for their livelihood. Ten of thousands of hectares of tropical forests have been cleared to make way for rubber plantations. Chemists have been able to combine other dienes to obtain synthetic rubbers. Some rubber products include latex products such as hand gloves, raincoats and other products used in battle against HIV/AIDS like condoms. The world largest use of rubber is in tyres, and most tyres contain both natural which with stands heat better, and one or more kinds of synthetic rubber.

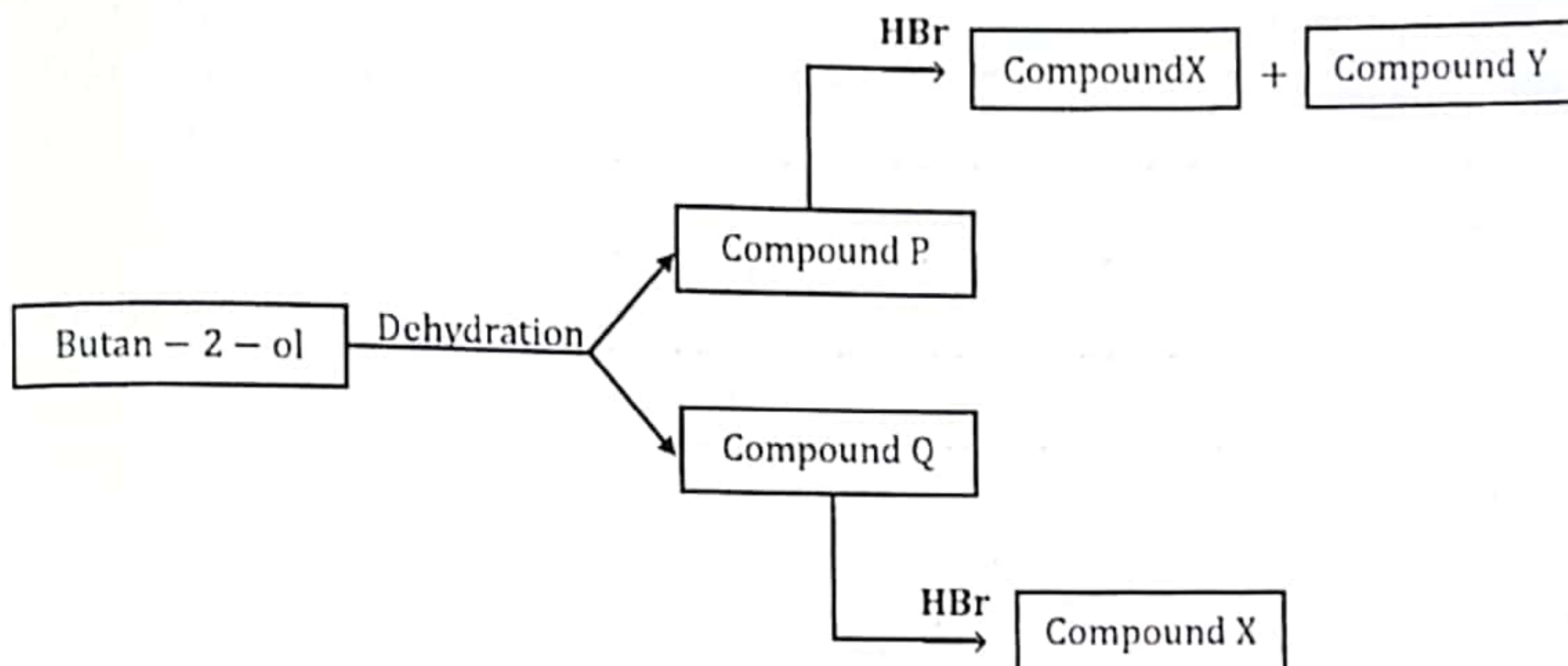
Answer the following questions:

- Is 2 - methyl - 1,3 - butadiene an example of a saturated or unsaturated hydrocarbon? Give a reason for your choice.
 - Write down structural formula of 2 - methyl - 1,3 - butadiene
- What type of polymerisation is involved in the production of synthetic rubber?

- c) With regard to the environment, mention at least two disadvantages of rubber and the production of rubber
- d) With regard to human life mention at least two benefits of rubber

Question 38

The flow diagram below shows the conversion of an alcohol into haloalkanes



- a) Name the type of organic reaction of which dehydration is an example
- b) To which homologous series do compounds P and Q belong?
- c) What type of reaction takes place when P is converted to compound X and Y as illustrated above
- d) Write structural formula of
 - (i) P
 - (ii) Q
- e) Which compound P or Q will be the major product? Give reasons for your choice
- f) Write down the structural formula of
 - i) X
 - ii) Y

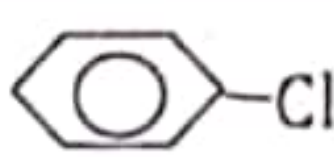
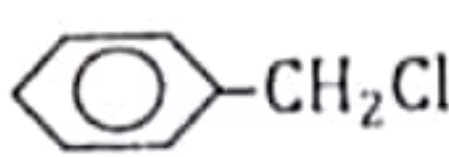
State which one is the major product between X and Y and state the rule you applied to make the choice.
- g) A learner indicates that he can convert butane - 2 - ol directly into compound X Give the chemical equation for such reaction

Question 39

Soap is manufactured by the hydrolysis of naturally- occurring compounds using sodium hydroxide. Name the type of compound present in soap and draw the structure of the organic by - product formed when these naturally occurring compounds are hydrolyzed to produce soap

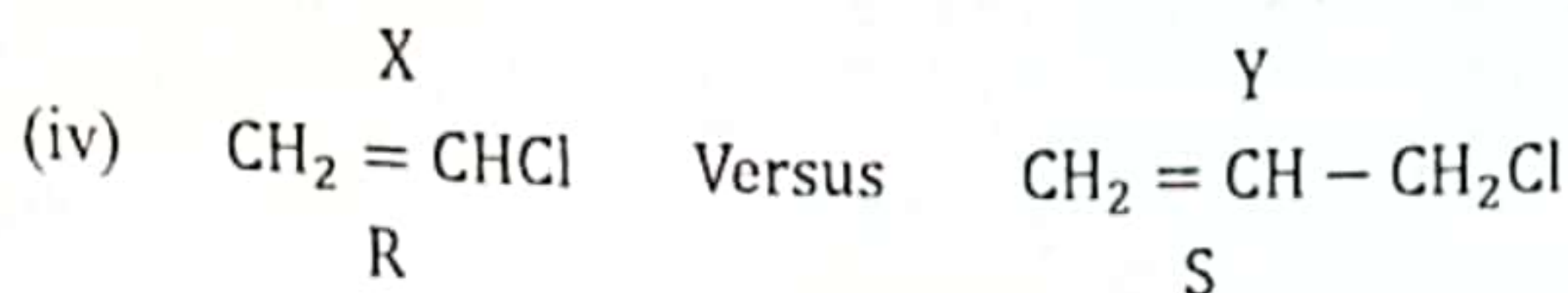
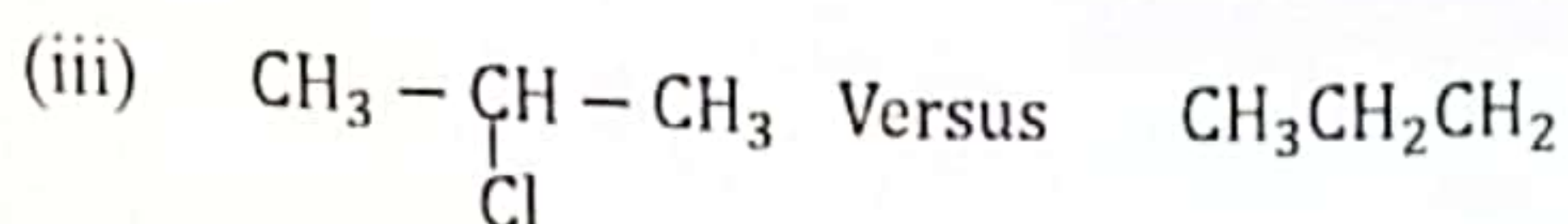
Question 40

Which of the following undergo S_N2 faster? Give reason for your choice

- (i)  Versus 

P
Q
- (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ Versus $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

A
B



Question 41

Haloalkane react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain

Question 42

Arrange the following compounds in order of increasing their acidic strength.

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol

Question 43

Generally aniline direct bromination gives tri-substituted product; to get mono-substituted product, what is to be done.

Question 44

Arrange the following compounds in order of increasing of their reactivity towards nucleophilic addition reaction.

HCHO, CH₃CHO, CH₃CHOCH₃

Question 45

Alcohols are weak acid than water Explain?

Question 46

The commercial ethanol is mixed with copper (II) sulphate and pyridine. Explain?

Question 47

Unlike phenols, alcohols are easily protonated Give reason

Question 48

Phenol react with bromine in the presence of carbon disulphide to give monobromophenol whereas with water gives tribromophenol. Explain.

Question 49

While a mixture of ortho and para nitrophenols is separated by distillation, name the isomer which is steam volatile. Give reasons.

Question 50

Carboxylic acids cannot give characteristic reactions of aldehydes and ketones though both are having carbonyl group- CO -, explain.

Question 51

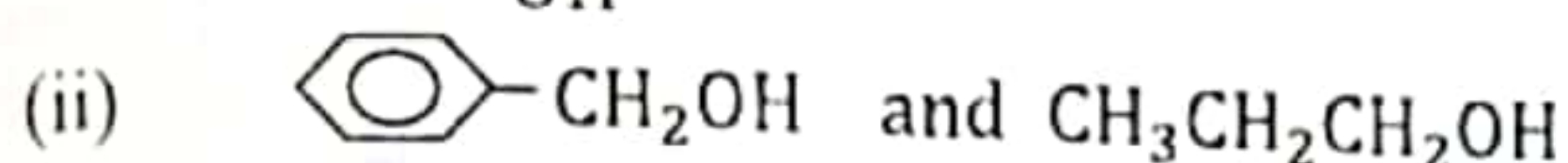
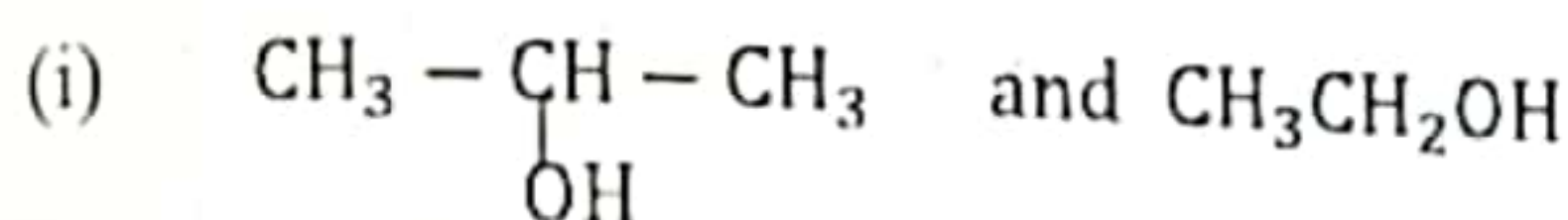
Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide. Why?

Question 52

During preparation of ester by reaction of carboxylic acids and alcohols, the ester formed distilled out as soon as it is formed. Explain.

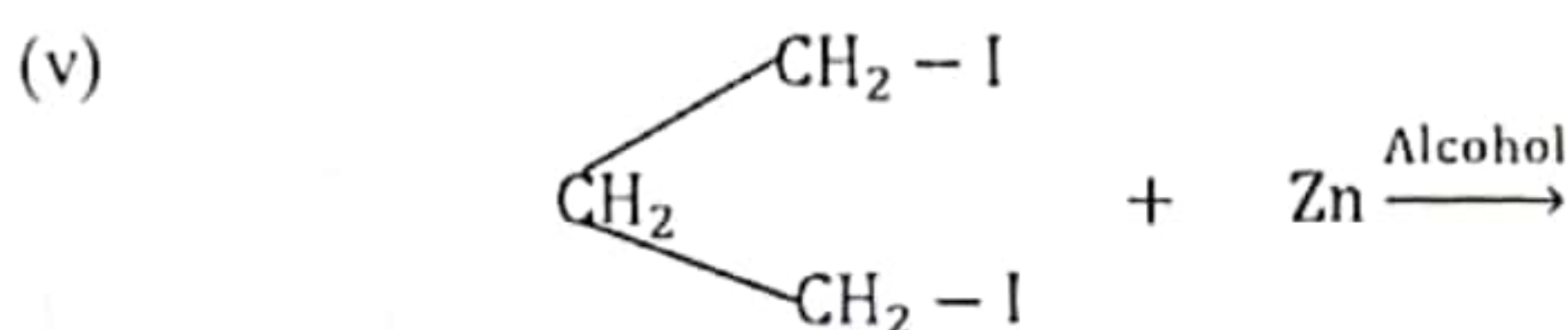
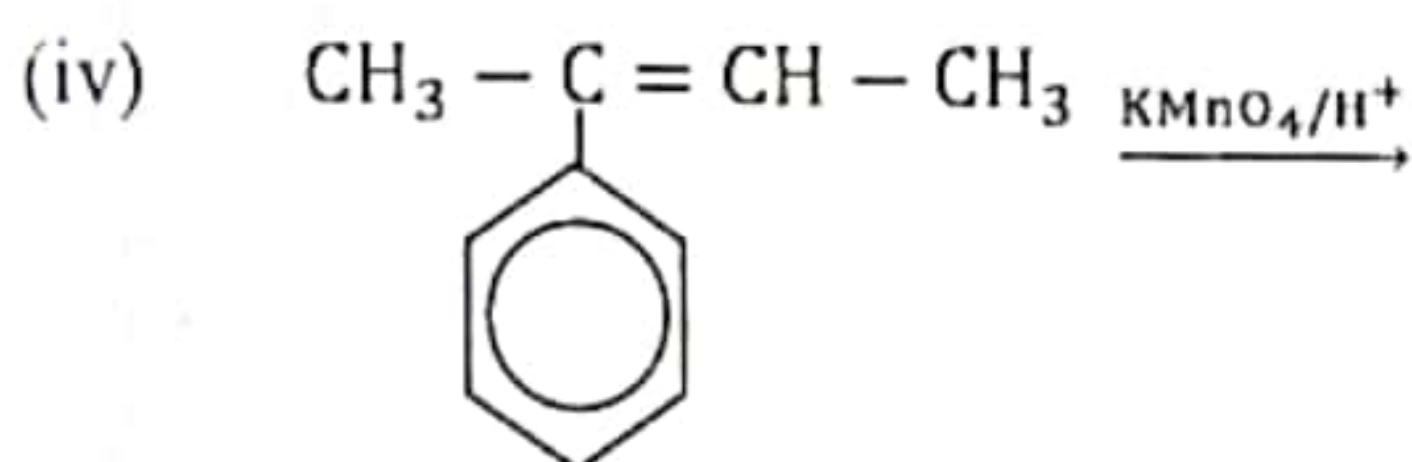
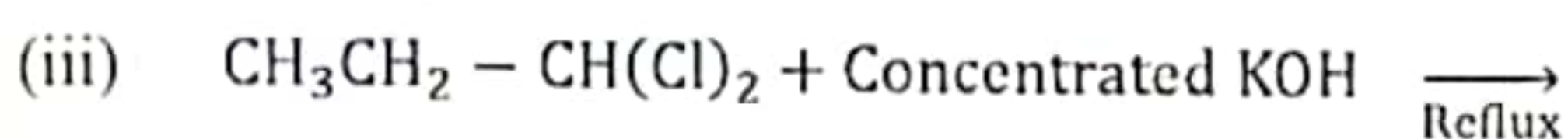
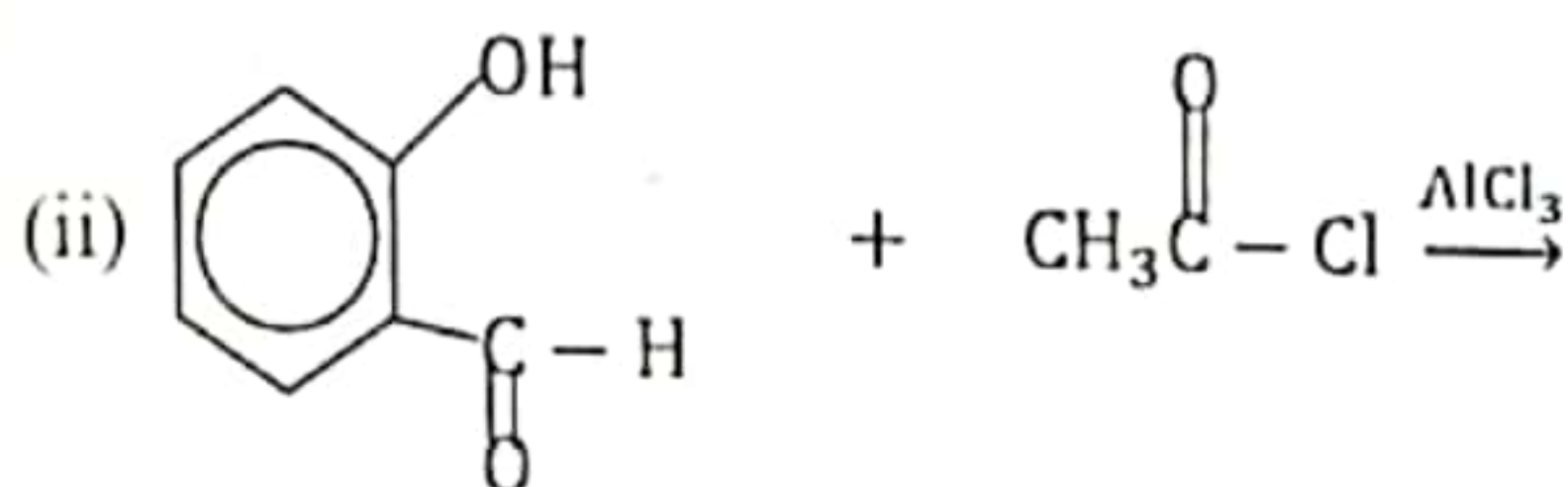
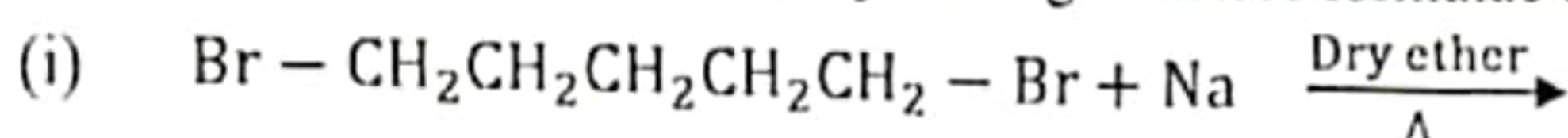
Question 53

For each of the following pairs of the compound, suggest one observable distinguishing chemical test in:



Question 54

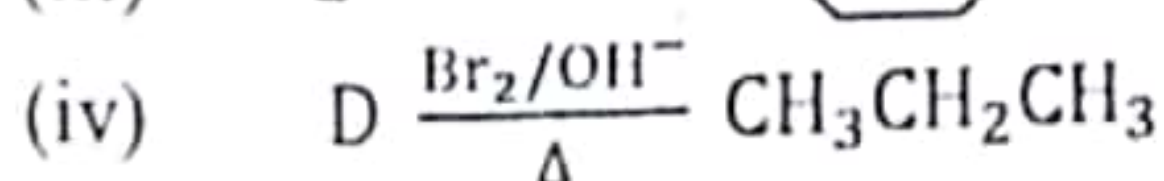
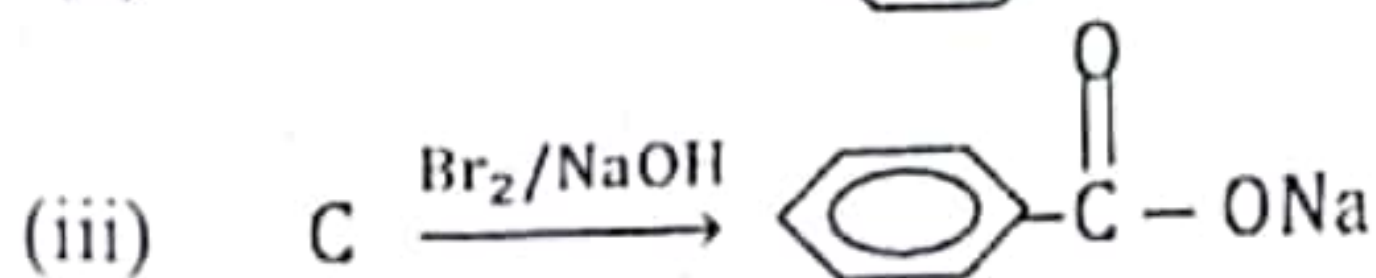
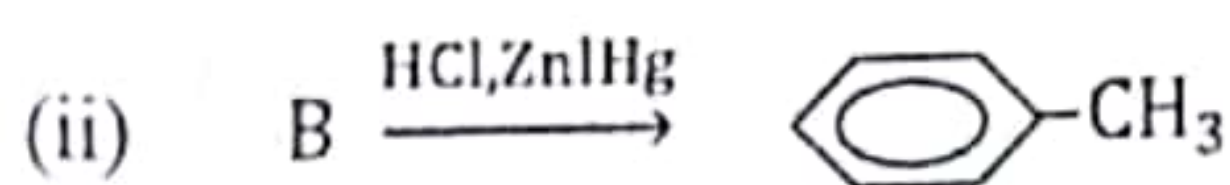
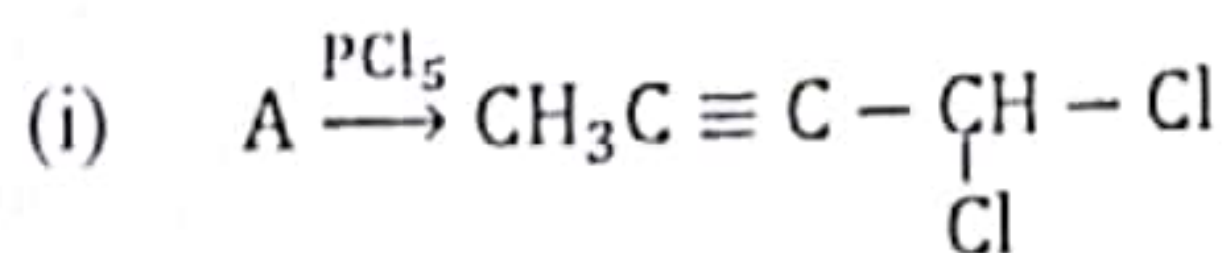
a) Complete the following reaction by writing structure formulae of products

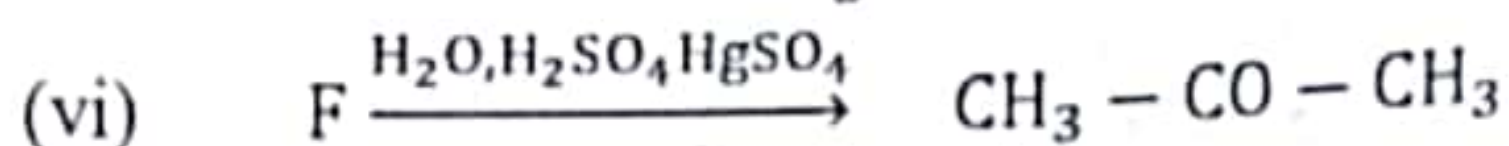
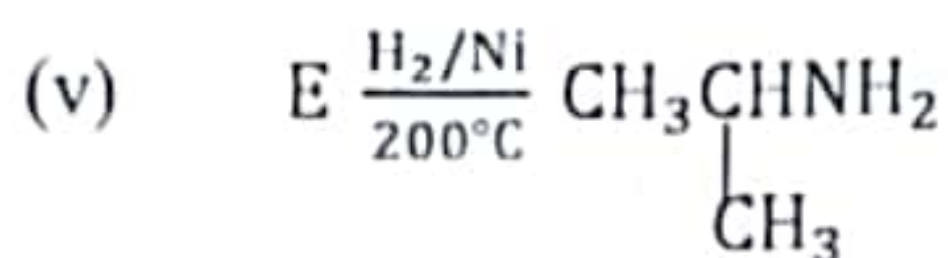


b) An alcohol B reacts with concentrated H_2SO_4 at 170°C to form alkene Q, Q reacts with ozone, zinc dust and water to give propanone and ethanal. Deduce structural formula of Q and B.

Question 55

Identify by giving Structural formula of organic compound A to F



**Question 56**

- a) Describe briefly with example the following terms
- Polymer
 - Monomer
 - Polymerisation
 - Homopolymer
- b) Co-polymer What do you understand by the term chain growth polymerisation?
- c) By considering the formation of polystyrene, explain what do you understand the following terms as applied in cationic addition polymerisation
- Initiation step
 - Propagation step
 - Termination step

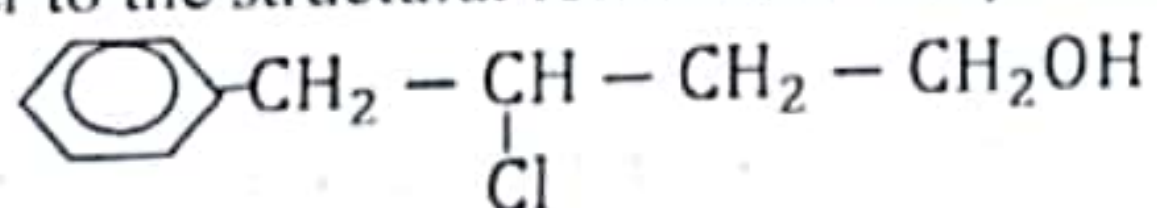
Question 57

Name a simple chemical test or reagent to distinguish between each of the following pair of organic compound.

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{Br}$
- (ii) $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{Cl}$ and $\text{C}_6\text{H}_5-\text{CH}_2\text{Cl}$

Question 58

Refer to the structural formula of compound A below



Write chemical equation to show the reaction which will take if compound A is mixed with

- Magnesium turnings in presence of dry ethyl ethoxide then warmed
- Concentrated sulphuric acid at 0°C
- Aqueous solution of sodium hydroxide at 25°C
- Chlorine gas and iron(III) chloride at 25°C
- Sodium ethoxide at 55°C
- Acetic and concentrated sulphuric acid then warmed
- Concentrated nitric acid and concentrated sulphuric acid at room temperature

Question 59

- a) Write the structural formula for each of the following compound
- Aspirin
 - Brady reagent
 - TNT
 - Hex - 2 - en - 4 - yne
- b) Describe the simple chemical tests that would distinguish between the following
- Pent - 2 - ene and n - pentane
 - pent - 1 - yne and pent - 2 - yne
 - Propanone and propanal

(iv) Benzene and phenol

Question 60

- a) Compound A on analysis by mass spectrometer was found to contain 60% carbon 13.3% hydrogen and 26.7% oxygen. The relative molecular mass of the compound was found to be 60.
- Calculate the molecular formula of compound A
 - Draw two possible displayed formula for isomers having this molecular formula
- b) A compound above was oxidised to B by refluxing with acidified sodium dichromate (VI). B is neither acidic nor reacted with Fehling's solution but it contained the same number of carbon atoms per molecule as A
- To what class of compound does B belongs
 - Hence deduce the correct formula of A and B

Question 61

Organic compound P, C_8H_8O , gave iodoform reaction and on vigorous oxidation yielded, Q, $C_7H_6O_2$, which was sparingly soluble in cold water after neutralisation. Q gives a buff precipitate with aqueous iron (III) chloride. Treatment of Q with phosphorous pentachloride gave R which reacted with concentrated aqueous ammonia to give a precipitate of S, C_7H_7ON . Prolonged treatment of S with phosphorous (v) oxide gave T which could be reduced to U, C_7H_9N . On reduction with alcohol under presence of sodium amalgam, P gave V, $C_8H_{10}O$. v gave positive iodoform test but did not give colouration with aqueous iron (III) chloride.

- Write the structural formula of substances P to V
- Write equation for
 - The reaction of P with iodine in alkaline condition
 - The reaction of R with water

Question 62

An organic compound 'Y' on treatment with ethyl alcohol gives carboxylic acid 'X' and a compound S. Hydrolysis of S under acidic condition gives X and Z. Oxidation of Z with $KMnO_4$ also gives X. X upon heating with $Ca(OH)_2$ gives F(C_3H_6O). F does not give Tollen's test and does not reduce Fehling's solution, but forms a 2,4 - dinitrophenylhydrazone. Identify Y, X, S, Z and F and write all reactions involved.

Question 63

Write equation to show how benzaldehyde reacts with:

- Sodium hydroxide solution
- Zinc amalgam and concentrated hydrochloric acid
- Toller's reagent
- Warm phenylamine
- Acidified potassium permanganate solution

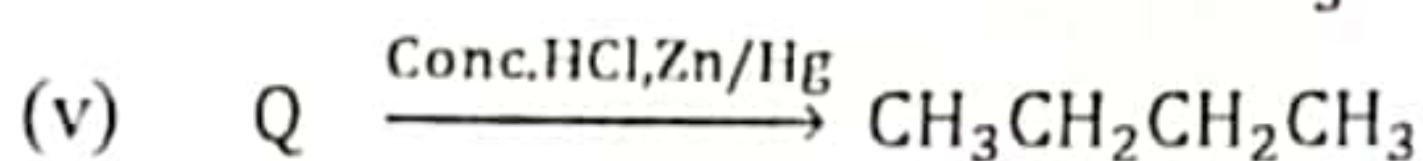
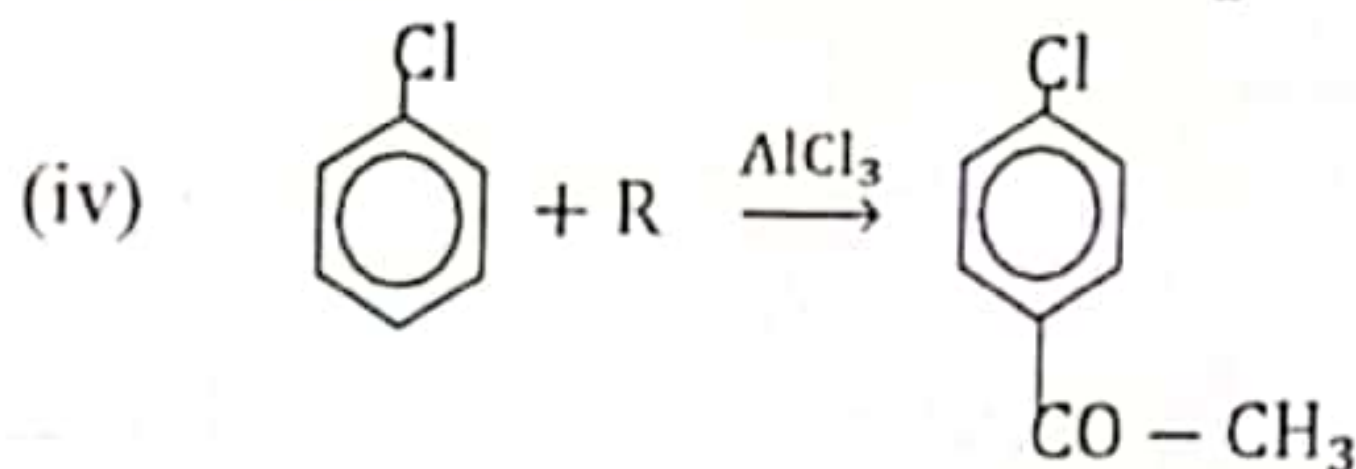
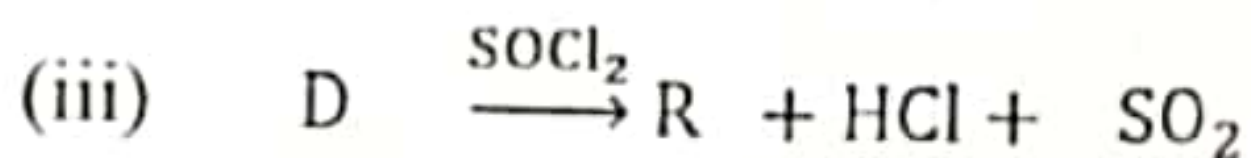
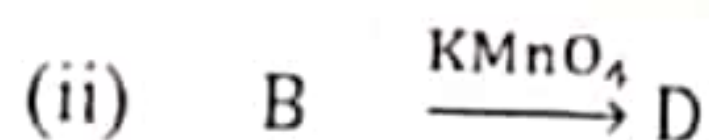
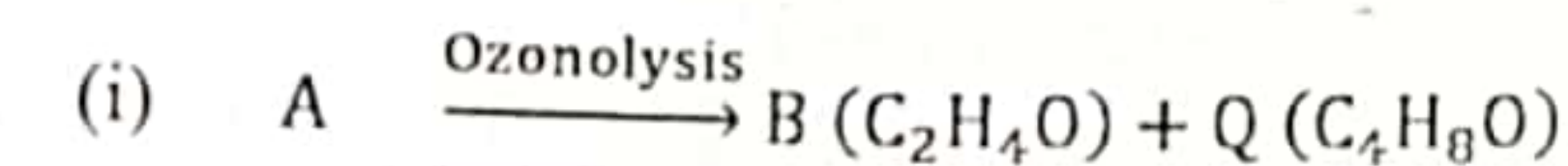
Question 64

Show how you can carry out the following conversions

- CH_3OH into CH_3COONH_4
- CH_3CH_2COOH Into CH_3COOH

Question 65

Study the following reactions and answer the questions below.



(i) Write the open structures of the compound A, B, Q, D and R

(ii) Give the systematic (IUPAC) names of the compounds A, B, Q, D and R.

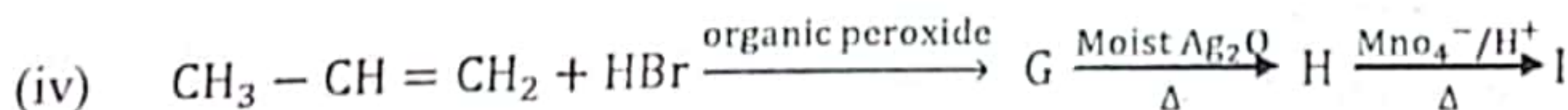
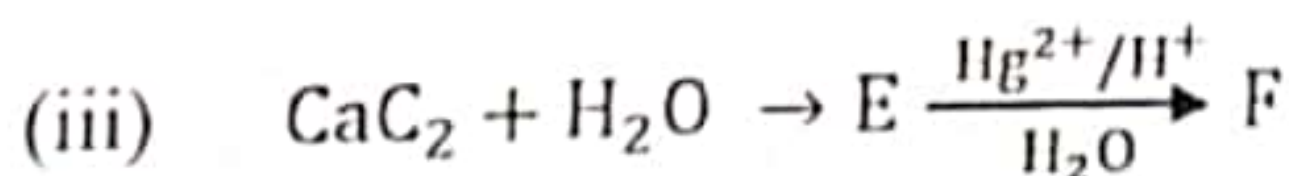
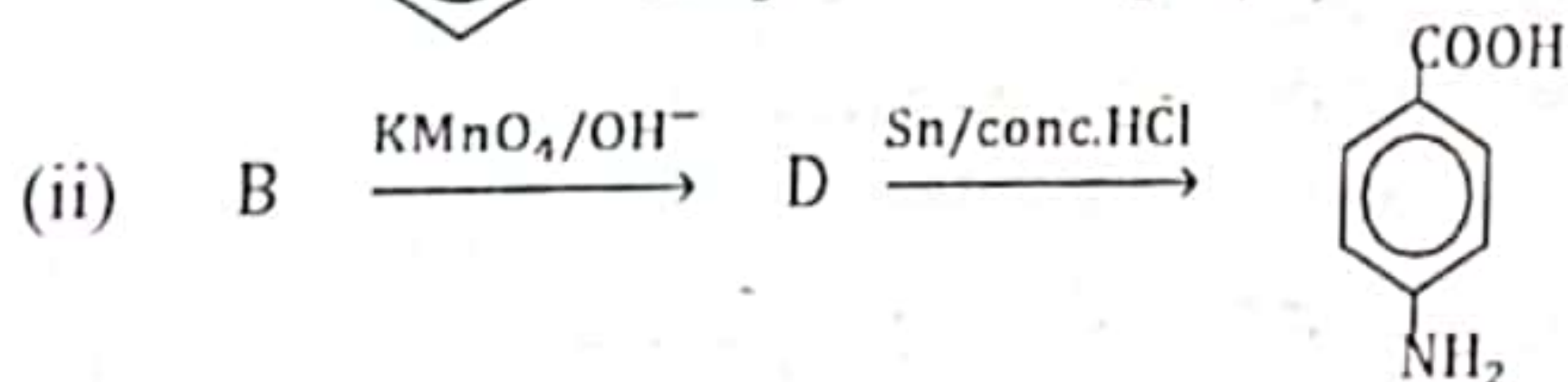
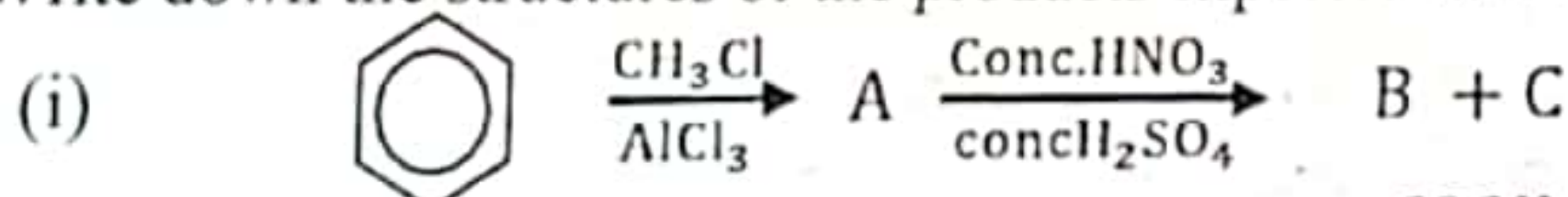
Question 66

a) In what sequence would you carry out the reactions;

(i) Chlorination

(ii) Nitration to obtain 3-chloronitrobenzene

b) Write down the structures of the products expected in the following reaction



Question 67

Give the structure of the product obtained when ethanal reacts with

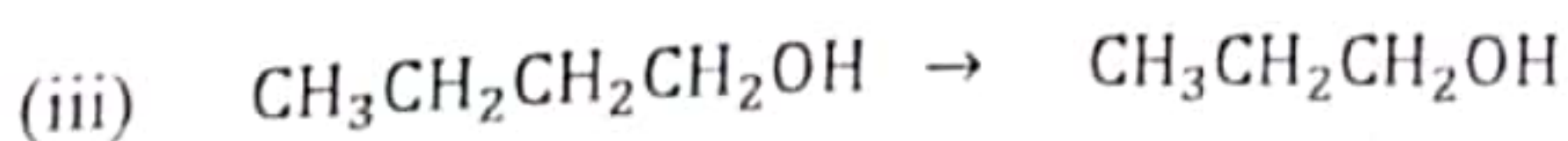
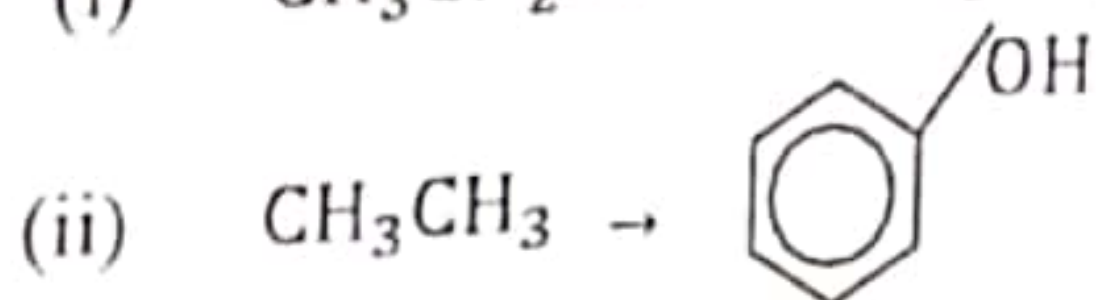
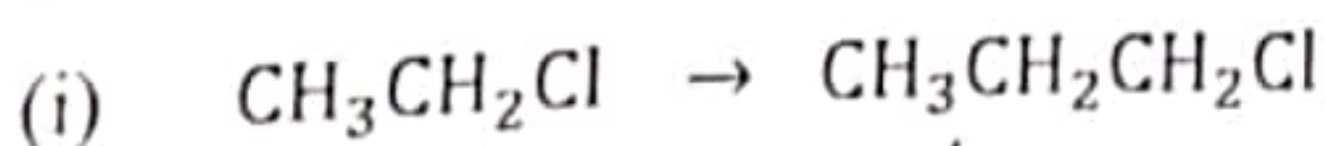
(i) HCN

(ii) An aqueous solution of NaOH in I_2

(iii) 2,4 - dinitrophenylhydrazine

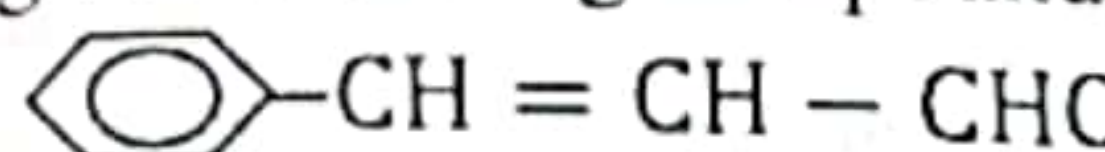
Question 68

Show how the following conversions may be effected (equation are not required)



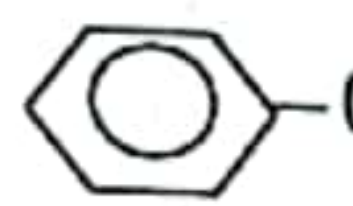
Question 69

Using the following compound

 as starting material mention which part of the compound will undergo the following types of reaction?

- Nucleophilic addition reaction
- Hydration
- Reduction
- Wolf-Kishner reaction
- Acylation

Question 70

Given the compound, methylbenzene (, Write equations to show what will happen when the compound is;

- Treated with chloromethane, CH_3Cl in the presence of aluminium chloride
- Treated with chlorine in presence of ultraviolet light
- Refluxed with potassium permanganate in the presence of an acid
- Burnt in excess of oxygen

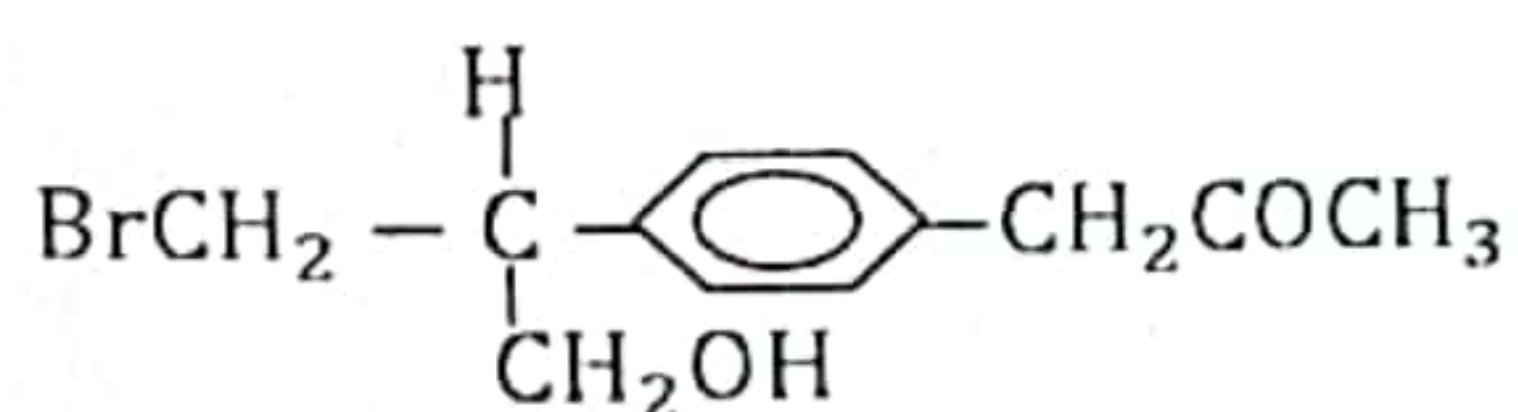
Question 71

Ketones and aldehydes are compounds with the same functional group. But ketone is less reactive than aldehyde

- What does the term functional group mean?
- What is the functional group of aldehyde and Ketones
- Why ketones are less reactive compared with aldehydes?

Question 72

By considering only functional groups present in the following compound

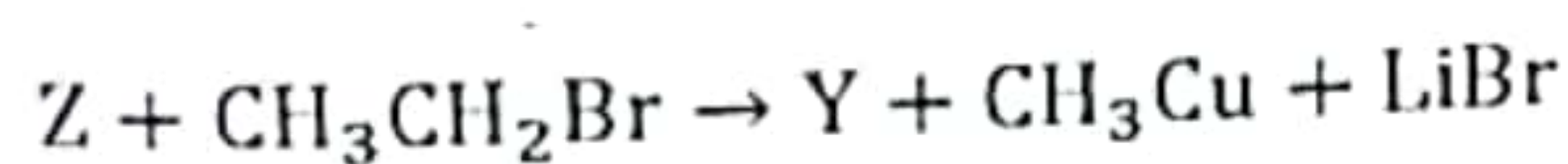
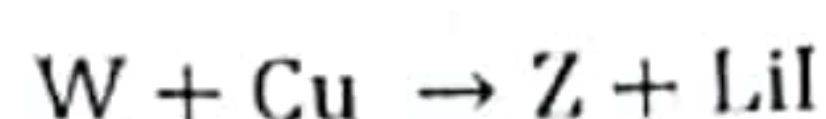
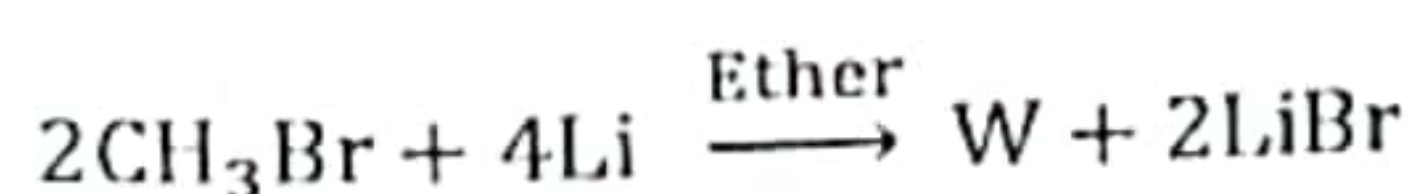


Predict the products when this compound reacts with

- Acidified KMnO_4 at $60^\circ\text{C} - 80^\circ\text{C}$
- Hydrogen gas and nickel at 140°C
- Phosphorous pentachloride
- A warm mixture of iodine and sodium hydroxide
- 2,4 - dinitrophenylhydrazine

Question 73

Consider the following reactions for synthesis of alkenes;



- Identify the unknown compound :W,Z,Y and give their names
- By using any other method, show how an alkane Y could be alternatively be synthesized.

Question 74

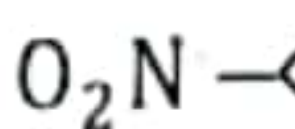
- a) Complete the following reactions and name the products
- (i) $\text{CH}_3\text{OH} + \text{NH}_3 \xrightarrow{\text{Al}_2\text{O}_3, 400^\circ\text{C}}$
- (ii) $(\text{CH}_3)_2\text{NH} + \text{CH}_3\text{Br} \rightarrow$
- (iii) $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{MgI} \xrightarrow{\text{H}_2\text{O}}$
- b) For each of the following given pairs of organic compounds identify which is more acidic than the other
- (i) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3COOH
- (ii) $\text{CH}_3\text{CH}_2\text{OH}$ and H_2O
- (iii) CH_3COOH and $\text{C}_6\text{H}_5\text{COOH}$
- (iv) $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{H}_5\text{COOH}$

Question 75

A compound C_3H_6O on treatment with methyl magnesium bromide followed by hydrolysis yielded an alcohol C_4H_8O which was not readily oxidised, but when drastically oxidised (under extreme conditions) it yielded only acetic acid and CO_2 . Give the structure of the original compound and of the alcohol.

Question 76

Identify the more acidic compound with reasons

- (i) CH_2ClCOOH versus CH_2BrCOOH
A B
- (ii) $\text{CH}_2\text{FCH}_2\text{COOH}$ Versus $\text{CH}_3\text{CHFCH}_2\text{COOH}$
C D
- (iii) CH_3 —— COOH Versus O_2N —— COOH
E F
- (iv)  Versus OH —— COOH
G H

Question 77

The following reaction is typical of certain functional groups in organic compounds

- A: Addition of bromine by reaction with solution of bromine in tetrachloromethane
- B: Formation of hydrogen chloride by the action of phosphorus pentachloride
- C: Evolution of nitrogen by the action of nitrous acid
- D: Formation of tri-iodomethane by the action of iodine and potassium hydroxide
- E: Formation of and alcohol by boiling with aqueous sodium hydroxide.

Select a reaction shown by the following compound and give equations where applicable.

- (i) $\text{CH}_3\text{CH}=\text{CHC}_2\text{H}_5$
- (ii) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (iii) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- (iv) $\text{CH}_3\text{CO}_2\text{CH}_3$
- (v) $\text{CH}_3\text{CO}_2\text{H}$

Question 78

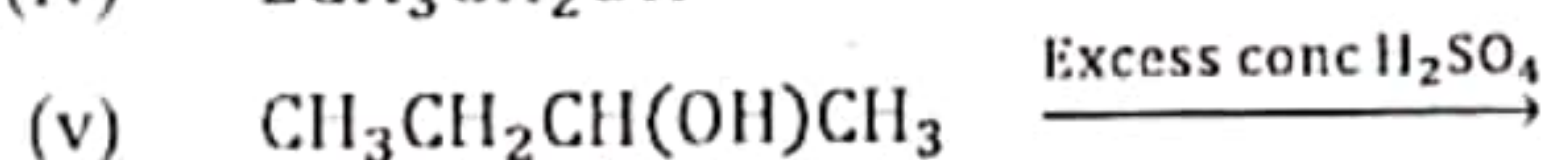
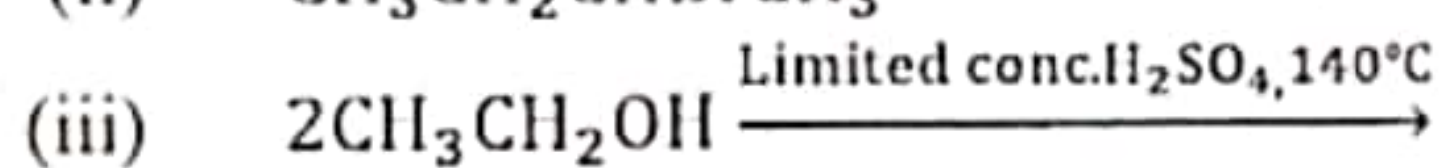
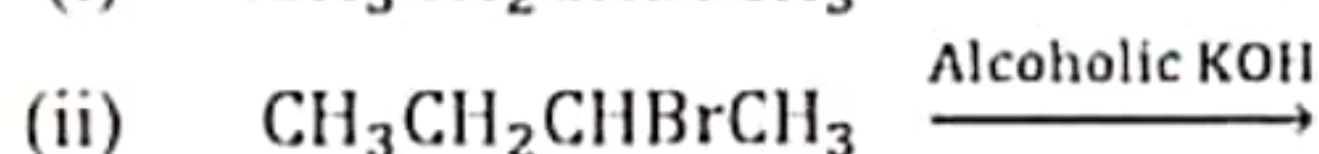
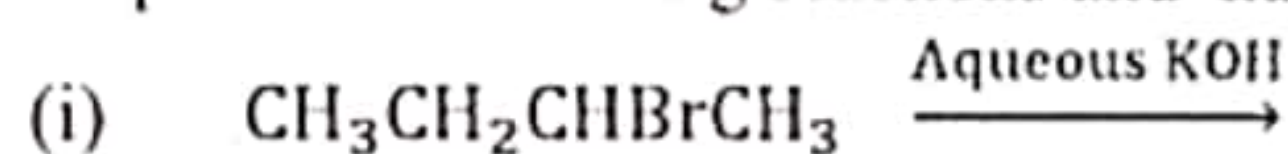
Compound A (C_6H_{12}) on ozonolysis followed by reductive hydrolysis gives B and C. Both B and C give a yellow-orange precipitates with Brady's reagent. B gives a positive tri-iodomethane test, while C does not. C gives positive silver mirror test with ammonical $AgNO_3(aq)$ while B does not. Give structural formula of A, possible structural formula of B and C.

Question 79

An organic compound P was boiled with dilute H_2SO_4 to produce an acid Q which was monobasic. Q was esterified with ethanol to give an ester R of molecular mass 150. Compound P can undergo reduction to form S. Give the structural formula of P, Q, R, and S.

Question 80

a) Complete the following reactions and name the product formed



b) With the help of chemical equations show how you can distinguish the following

(i) 1-butanol from 2-methyl-2-propanol

(ii) 2-butanol from 2-methyl-2-propanol

(iii) 1-Propanol from ethanol

(iv) 2-chloropentane from 1-chloropentane

(v) 2-butanone from 3-pentanone

Question 81

Indicate any reaction involving either side chain or the aromatic ring which occurs between phenylethene and

(i) H_2/Pt at $25^\circ C$

(ii) H_2/Pt at $200^\circ C$

Will the unsaturated side chain activate or deactivate the aromatic ring?

Question 82

Dehydration of an alcohol C_4H_9OH provides a hydrocarbon Y, C_4H_8 . When Y is treated with trioxxygen followed by water hydrolysis, only one product is formed which is Z.

d) Write all aliphatic structural isomers of Y

e) Identify Y and Z

f) Write equation for all chemical reactions involved

Question 83

0.64 g of CaC_2 reacted with water giving 200cm^3 of C_2H_2 at $27^\circ C$ and 1 atmosphere. Calculate the percentage purity of calcium carbide in the sample.

Question 84

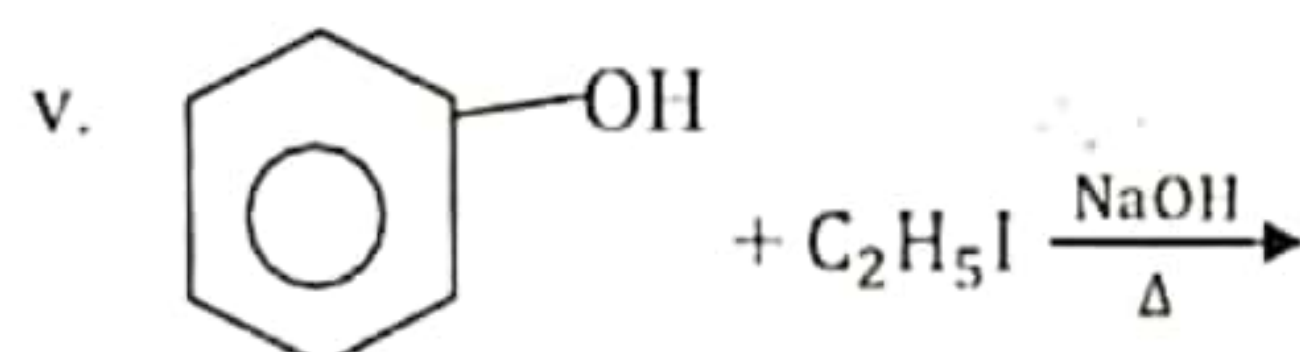
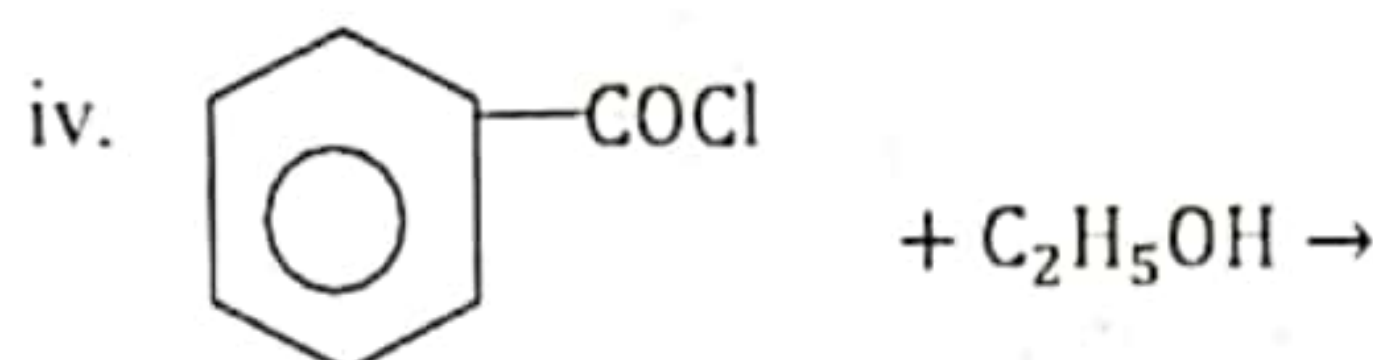
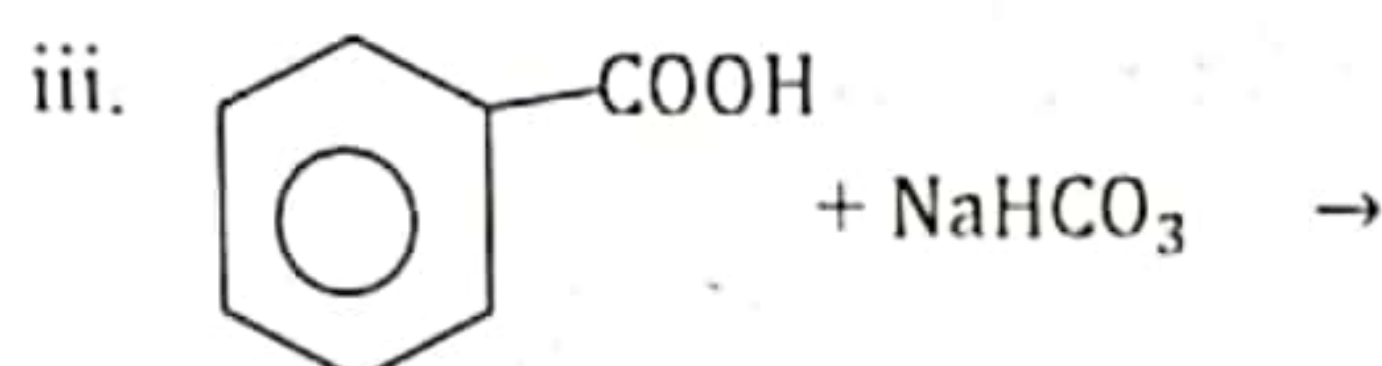
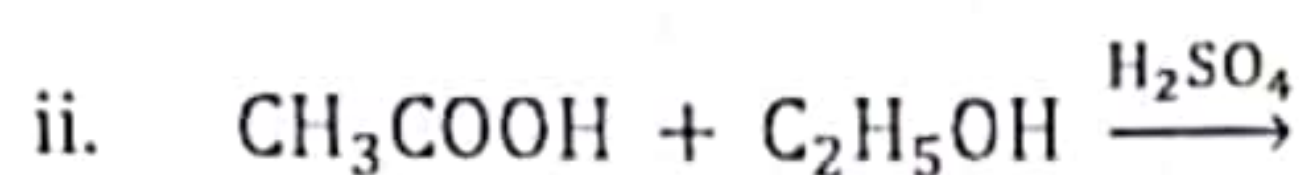
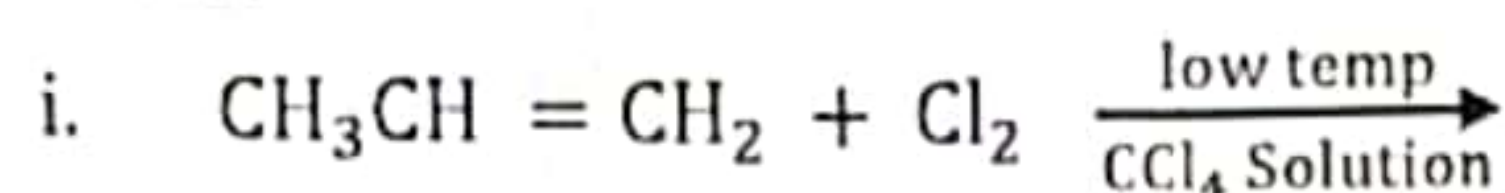
Consider the polymerisation of ethane using organic peroxide, $\text{CH}_3 - \text{O} - \text{O} - \text{CH}_3$ as polymeric inducer, in presence of ultraviolet light. If the polymer formed was found to have the molar weight at 52926g/mol. Calculate the number of monomer used to form such a polymer.

Question 85

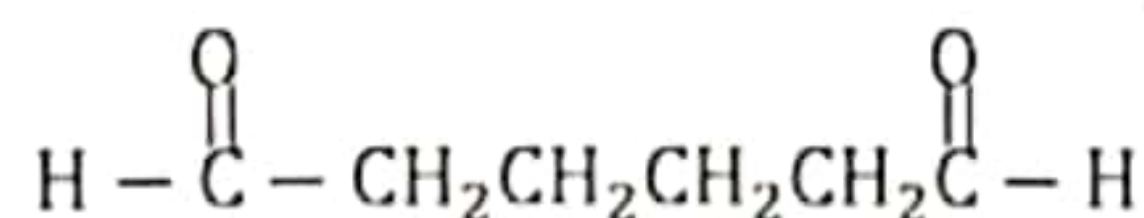
(a) Gives one chemical test to distinguish one compound from the other for each of the following pairs of organic compound

- But - 1 - yne and But - 2 - yne
- $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{OH}$
- $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_3\text{COH}$

(b) Indicate the structural formula and name(s) of the product(s) of each of the following reactions.



(c) A hydrocarbon of formula C_6H_{10} absorbs only one mole of hydrogen (H_2) upon catalytic hydrogenation, upon ozonolysis followed by reductive hydrolysis the hydrocarbon yield.

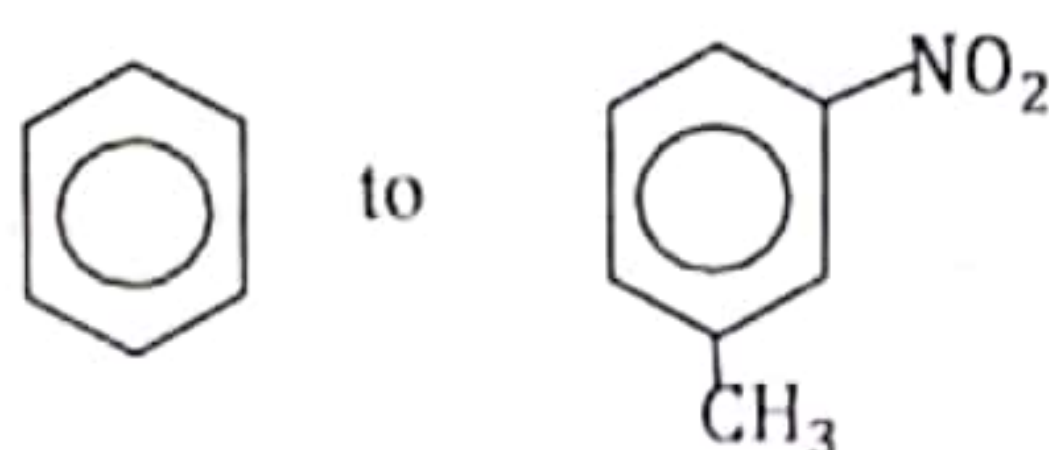


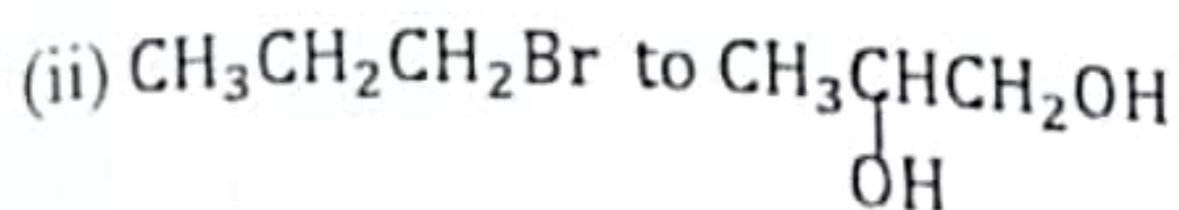
What is the structure of hydrocarbon? Explain clearly how you get your answer.

Question 86

a) By indicating the conditions and reagents used, show how the following conversions may be effected.

(i)

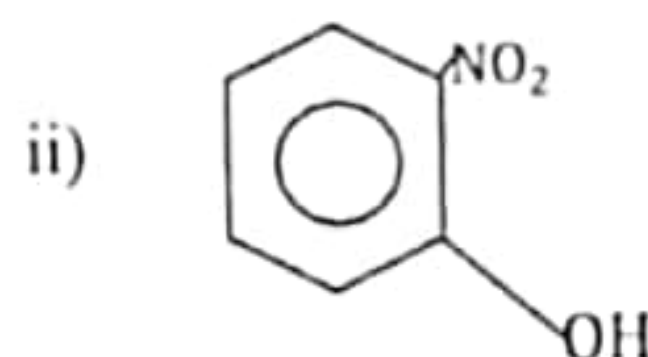
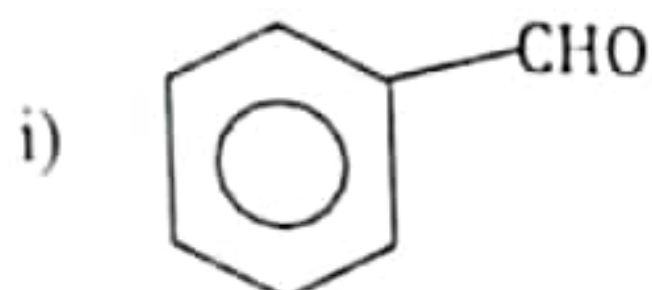




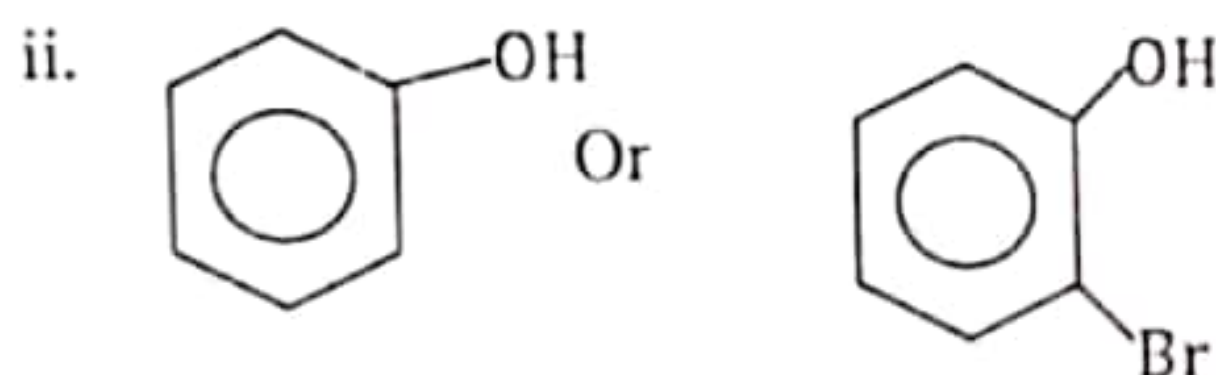
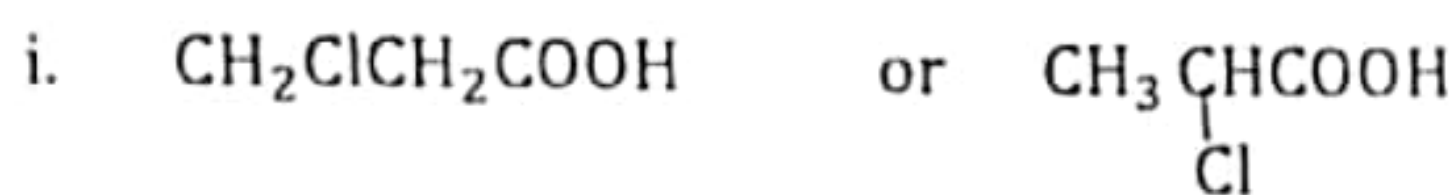
- b) A compound S is composed of 64.86% C, 13.5% H and 21.64% O. S reacts with PCl_5 to form compound P and a gas Q which produces dense white fumes with aqueous ammonia. S also reacts with a mixture of iodine and sodium hydroxide solution to form sodium salt R and triiodomethane.
- Determine the empirical formula of S.
 - Give the molecular formula of S if its molecular mass is 74.
 - Give the structures formula of five possible isomers of S.
 - Name the compound S, P, Q and R
 - Write the chemical equation for the
 - Reaction between S and PCl_5
 - Reaction between S and the mixture of I_2 and NaOH .

Question 87

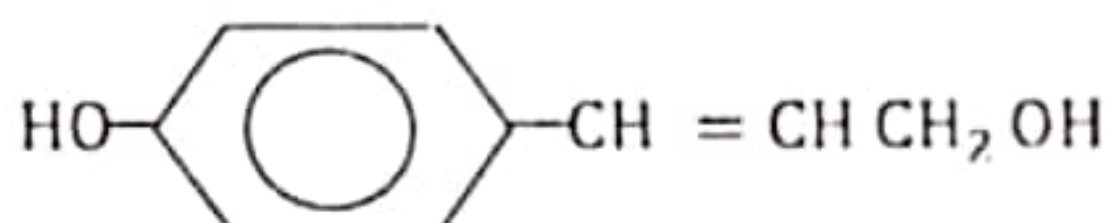
- a) Give the structure formula of the following compounds
- methyl phenyl ether
 - methanol
 - Propanone
 - 3-phenylpentene.
- b) Give the name and draw the structure of the product(s) formed in the mononitration of.



- c) For each of the following pairs of acids indicate which one is stronger? Give reasons for your choice.



- d) Write balanced chemical equations for the reaction of the compound



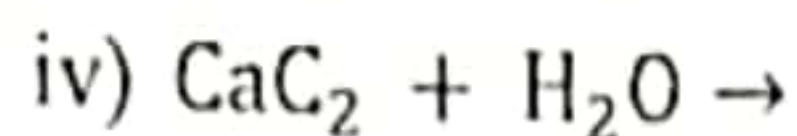
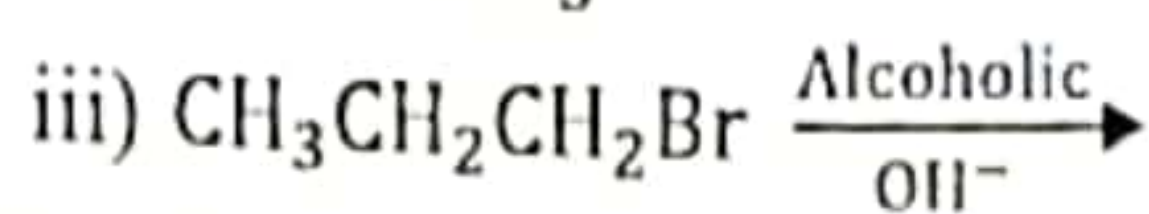
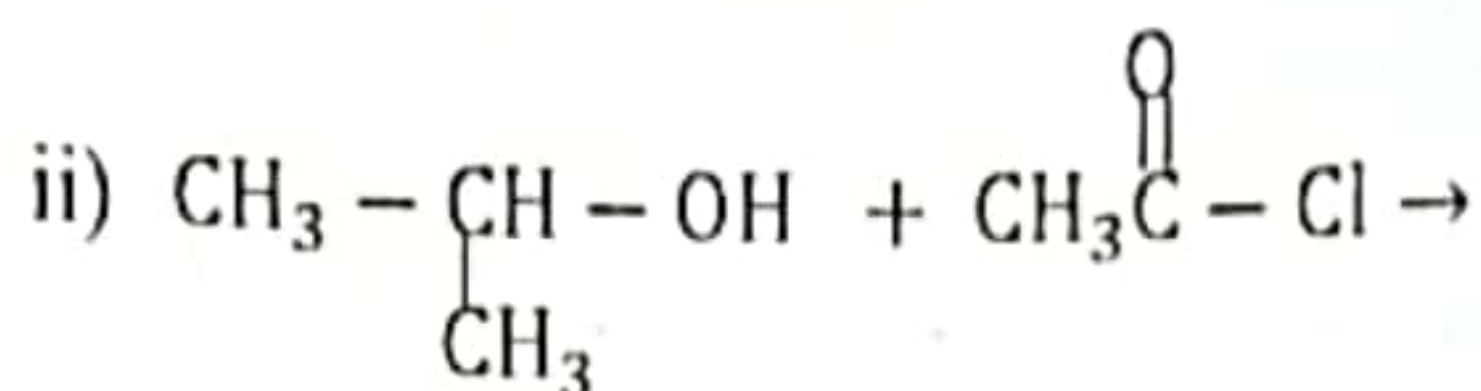
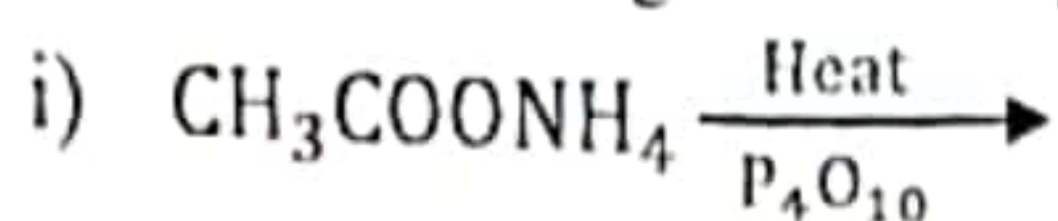
With

- Excess sodium metal
- Dilute alkaline KMnO_4
- Hydrogen and finely divided nickel
- Acetic acid under presence of concentrated H_2SO_4

Question 88

- a) An electrophilic substitution reaction in phenyl amine occurs in the ortho and para positions while in nitrobenzene it takes place at the meta position. Explain.

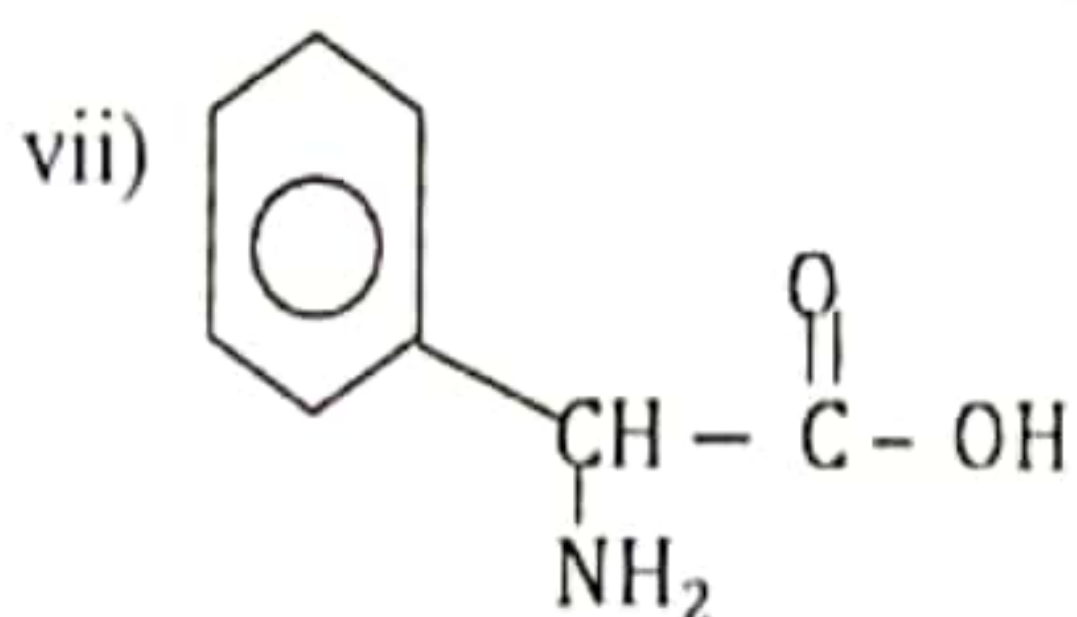
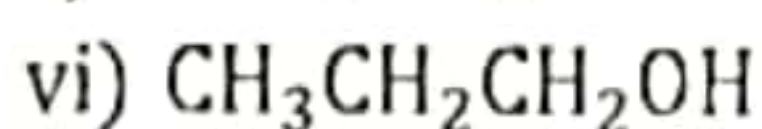
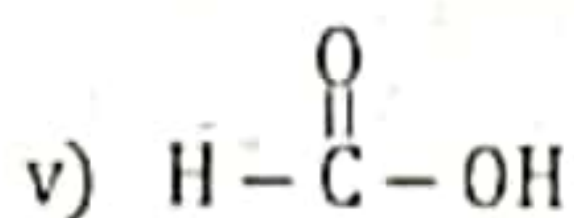
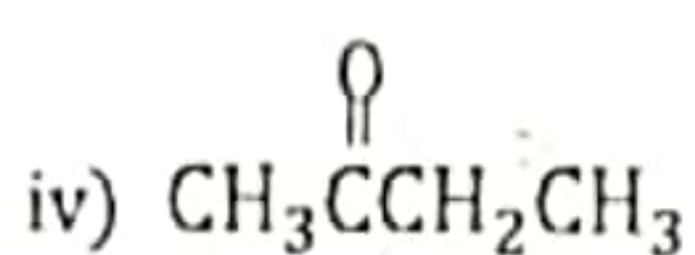
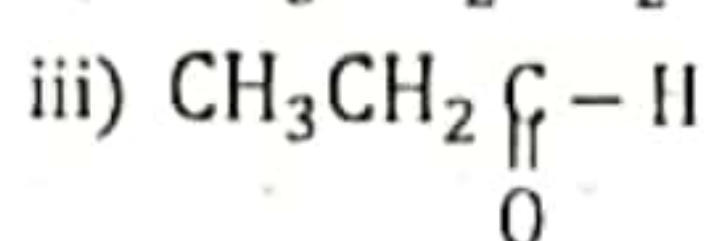
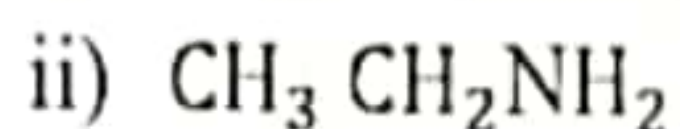
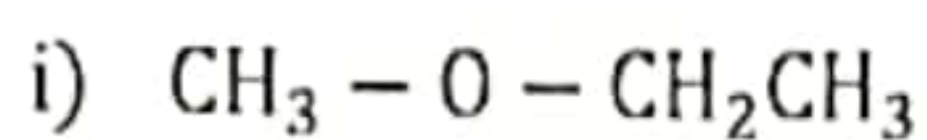
b) Complete the following reaction equations.



c) Briefly explain the meaning of and give one example in each case;

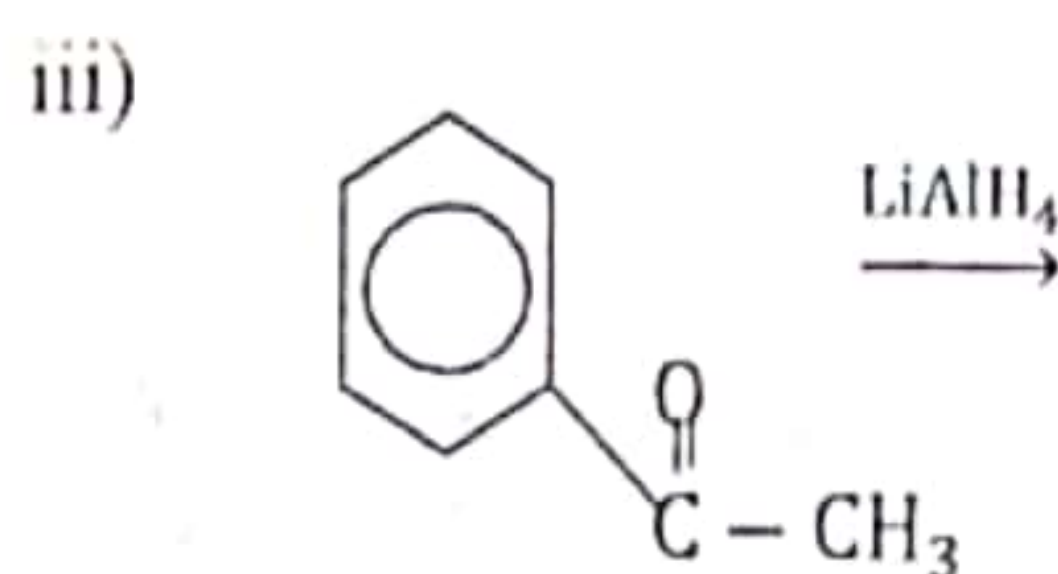
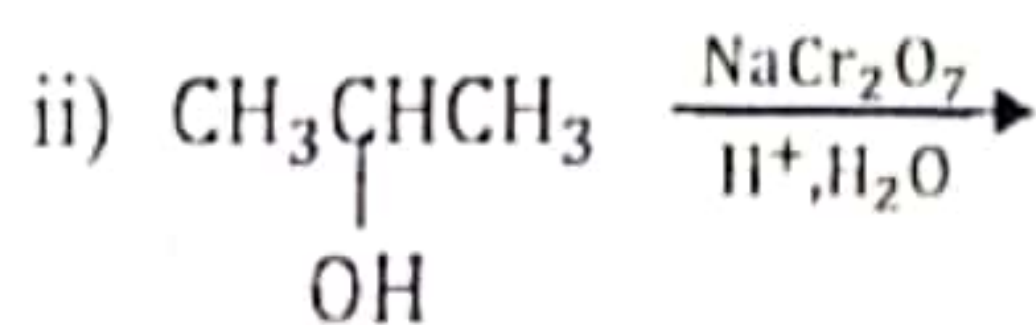
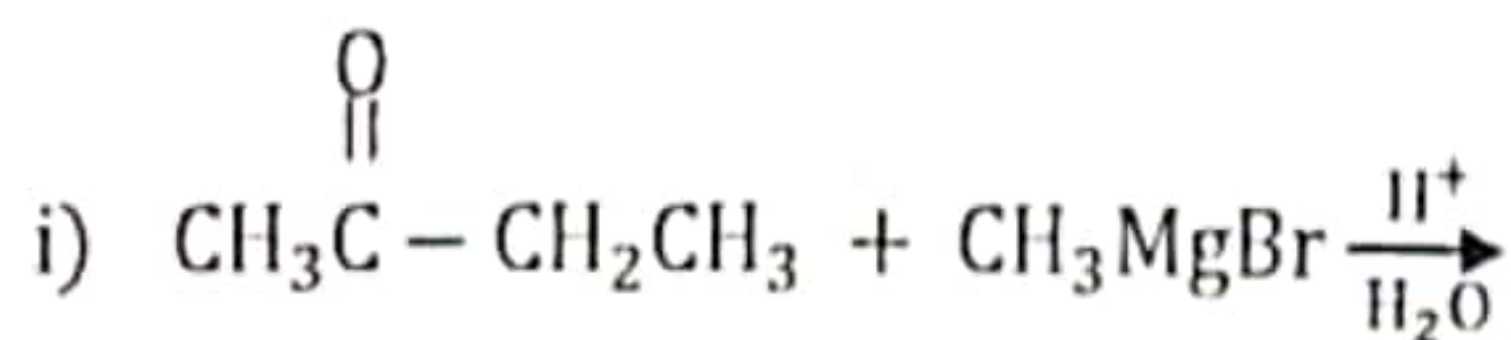
- Aldol condensation
- Addition reaction
- Organic substitution reaction
- Elimination reaction.

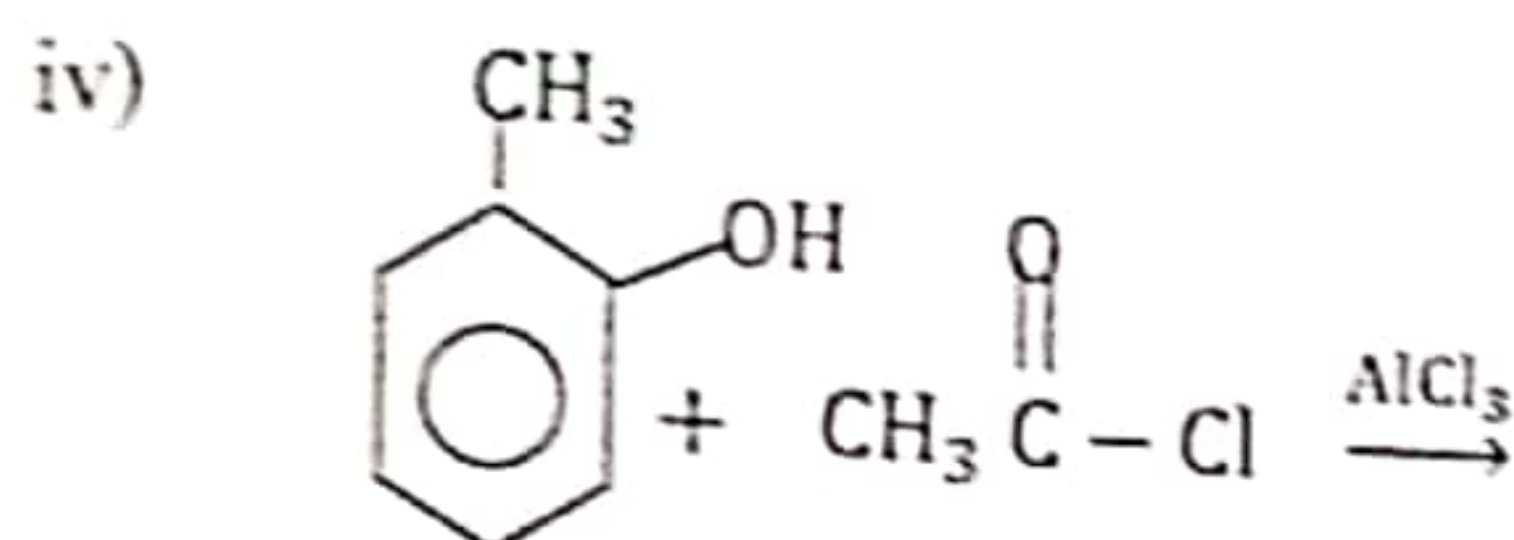
d) Classify each of the following molecules as alcohol, aldehyde, ketone, carboxylic acid, amine or ether.



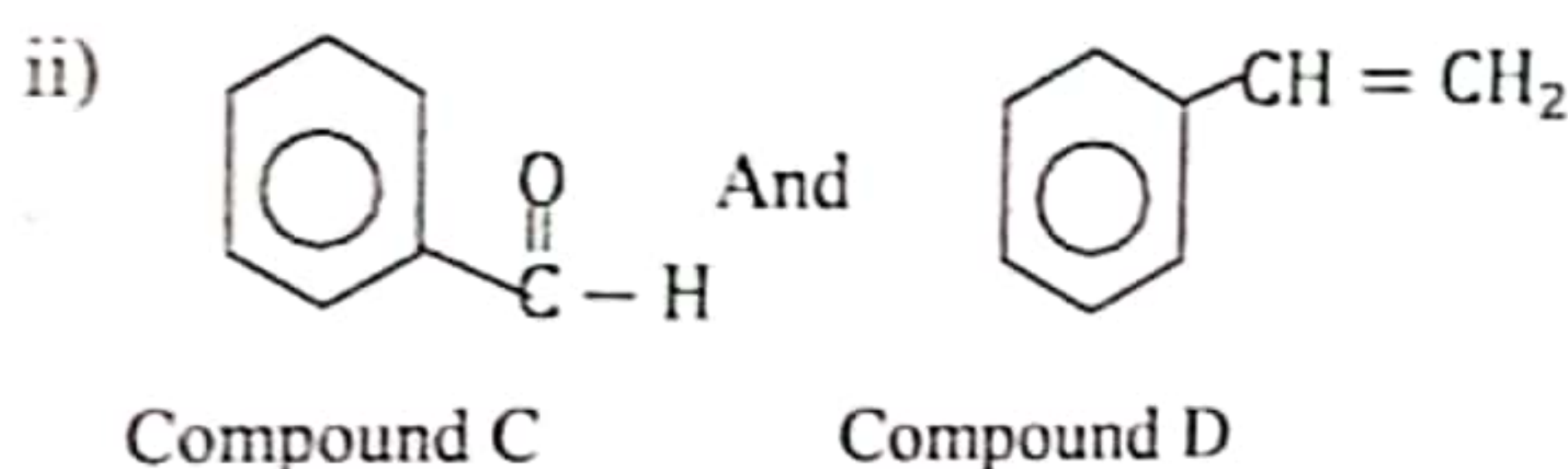
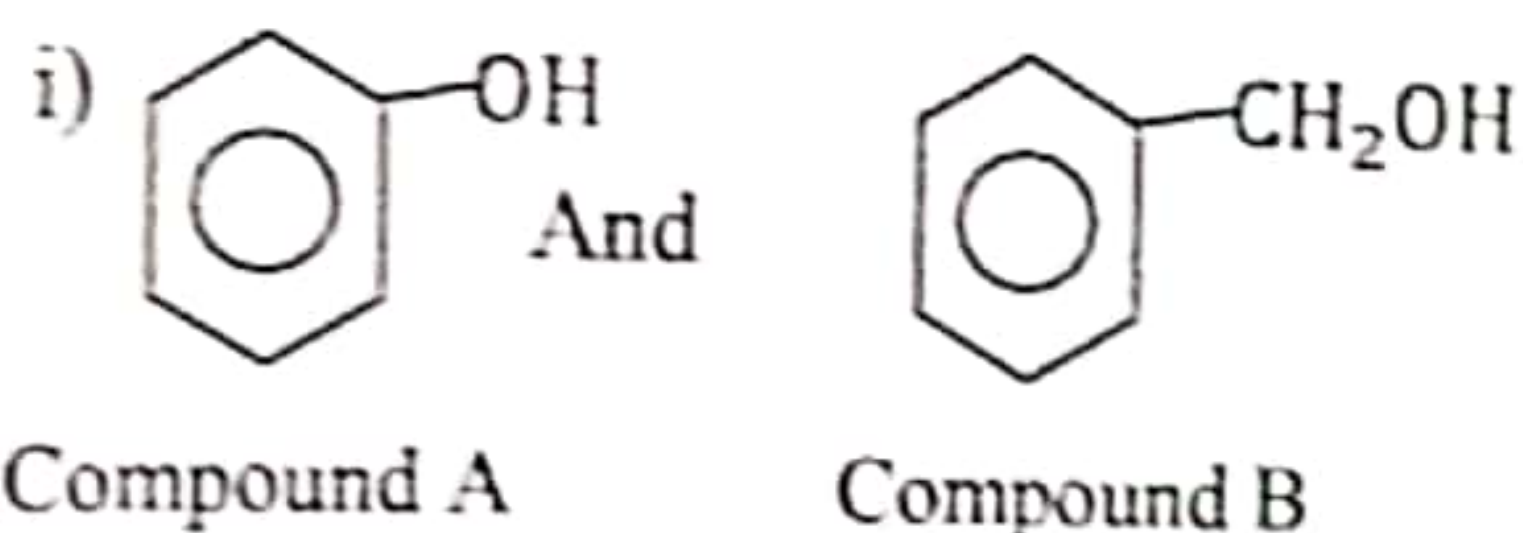
Question 89

a) Write the structure of the major organic product of the following reactions





b) What chemical test would you carry out to distinguish between the following compounds?



c) Give reasons to explain the following observations:

- Benzyl chloride reacts with aqueous silver nitrate to produce white ppt of silver chloride but chlorobenzene doesn't.
- 2, 2-dichloroethanoic acid is less acidic than 2, 2-difluoroethanoic acid.
- Pentan-2-one give positive iodoform test but pentan-3-one doesn't.
- 1-butyne produces white precipitate with ammonical silver nitrate but 2-butyne doesn't.

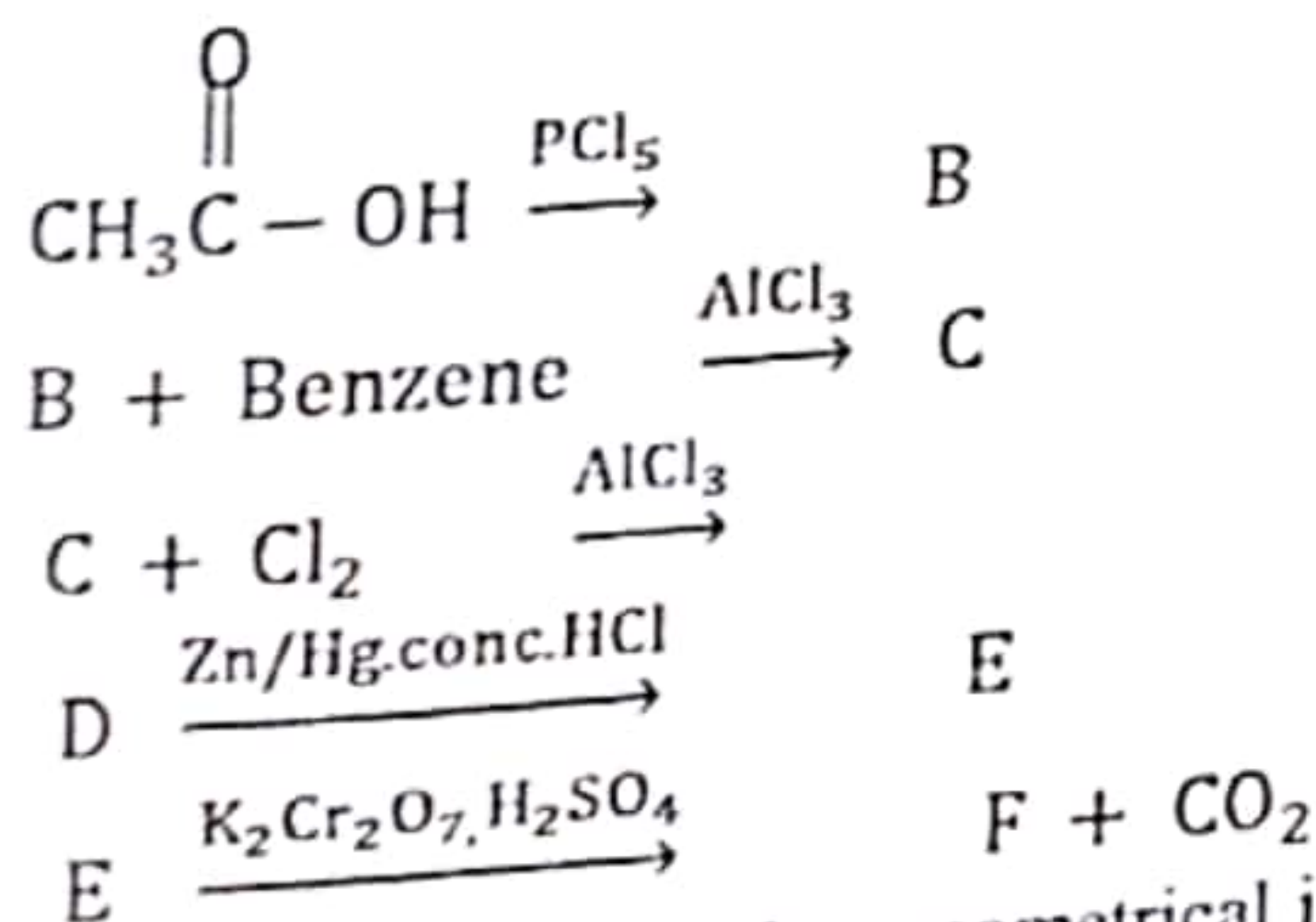
Question 90

a) Give the structural formula of the following compounds

- 1-chloro-3-Phenylpropan-2-one
- (1-bromoethyl)ethanoate
- Sodium 3-methyl benzene carboxylate
- Methoxy ethane

Question 91

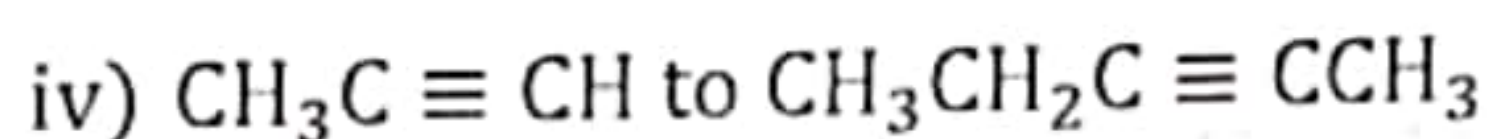
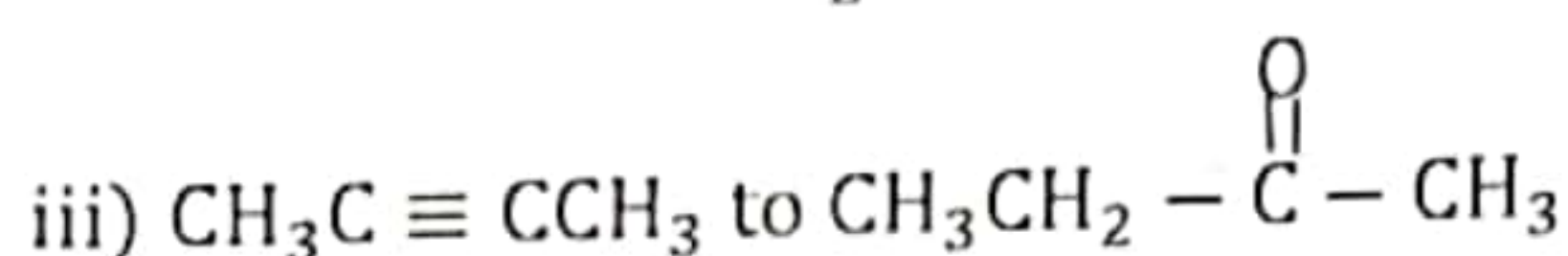
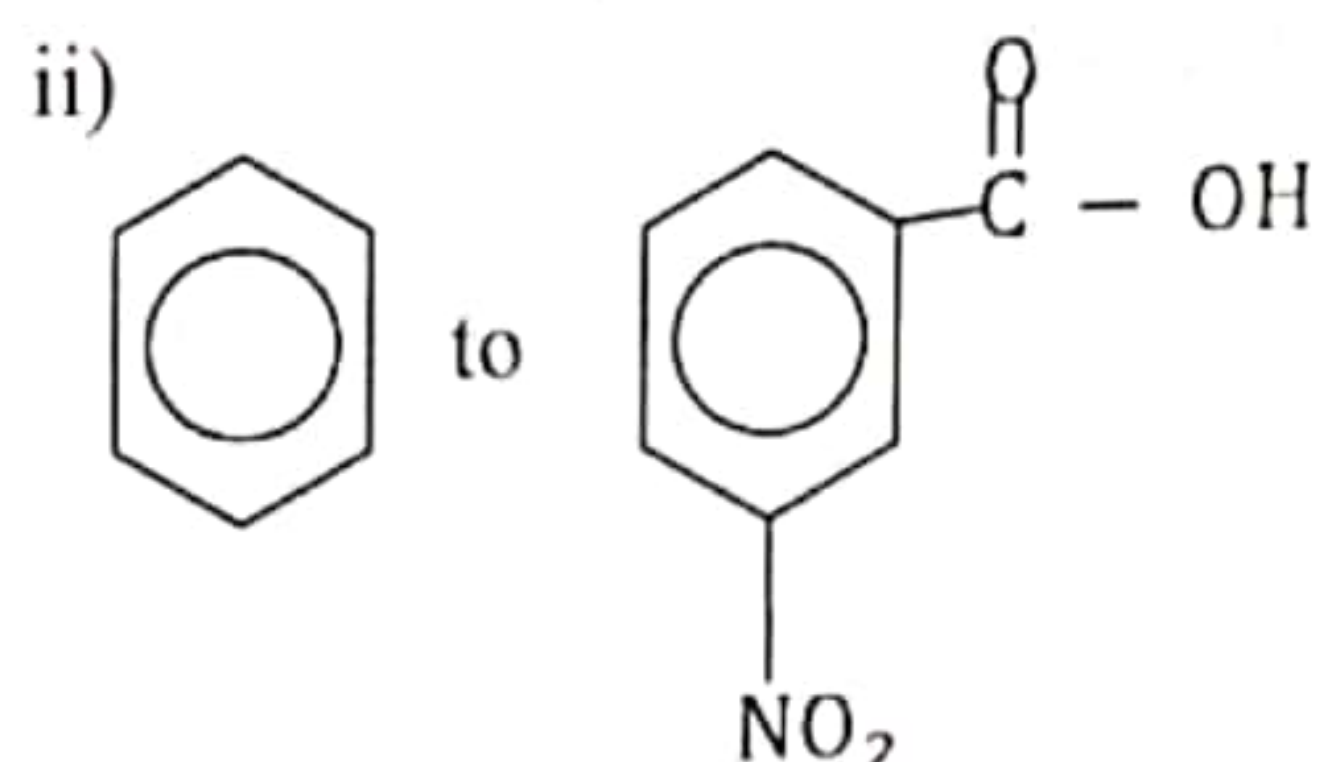
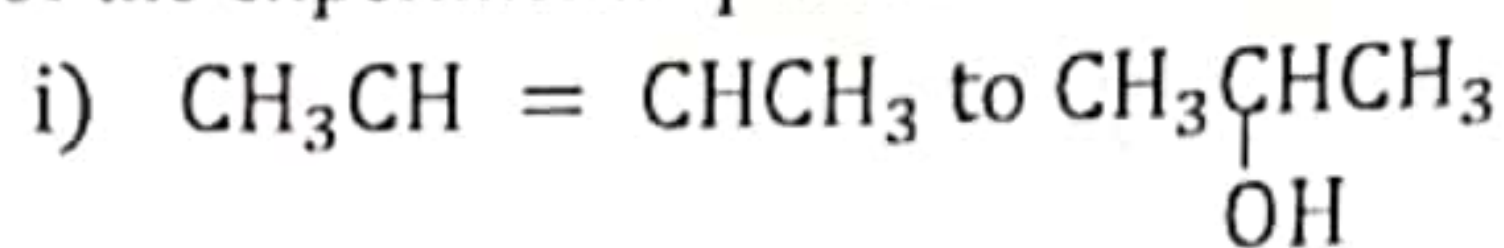
a. Study the following synthetic pathway and identify the compound B, C, D, E and F by drawing their open structures.



b. A hydrocarbon R which has geometrical isomers was found to contain 85.7% C and its vapour density was 28. R reacted with HCl to give compound S which easily reacted with NaOH to give compound T. Compound T was easily oxidised by hot acidified KMnO_4 solution to give compound U. Compound U had a positive iodoform test, it reacted readily with Brady's reagent but was not able to reduce Tollen's or Fehling's solutions. Identify R, S, T and U.

Question 92

- a. Outline how the following conversions can be affected; use not more than four steps. (Details of the experimental procedures are not required)



- b. Salicylic acid, 2-hydroxybenzoic acid is an analgesic which can irritate the stomach. However its ester, aspirin is less acidic and less irritating. Aspirin is easily hydrolysed in the alkaline condition of the stomach to 2-hydroxybenzoate which dissolves in the blood stream.

- Write the structure of Salicylic acid
- Write the structure of aspirin

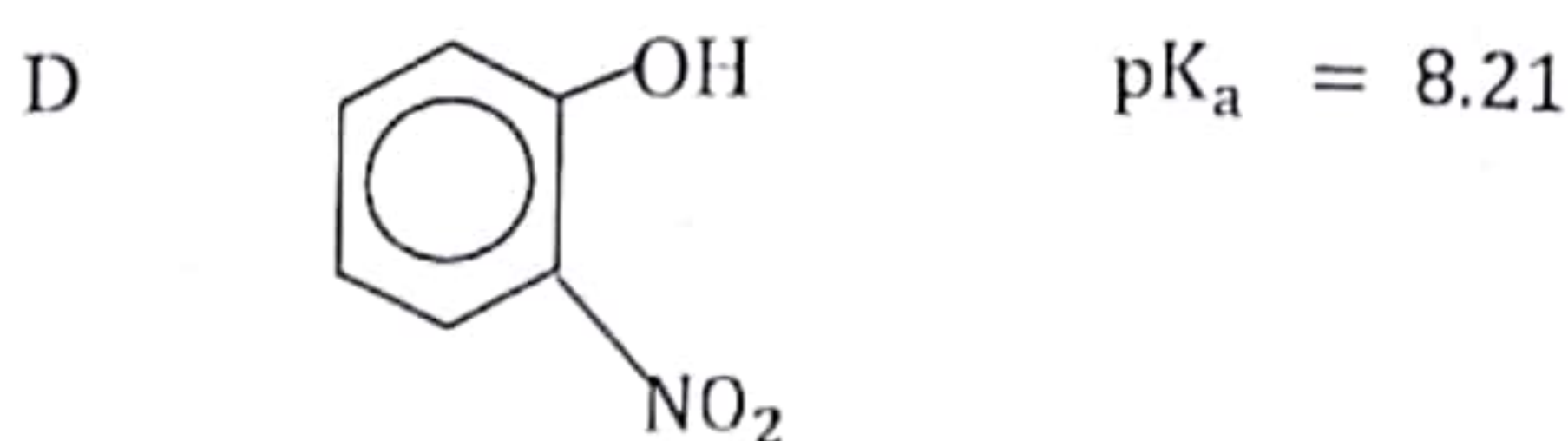
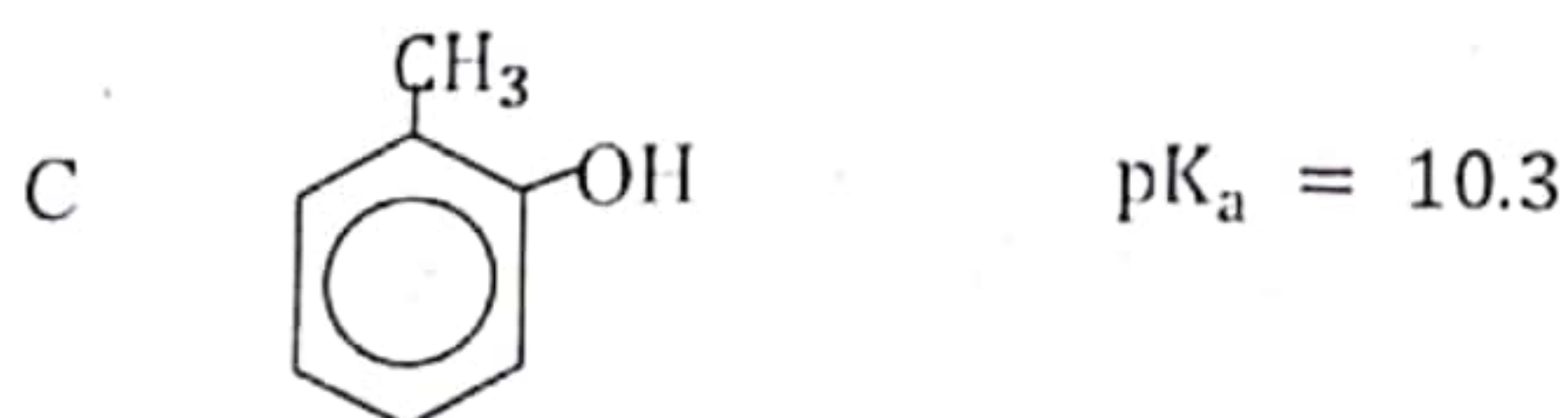
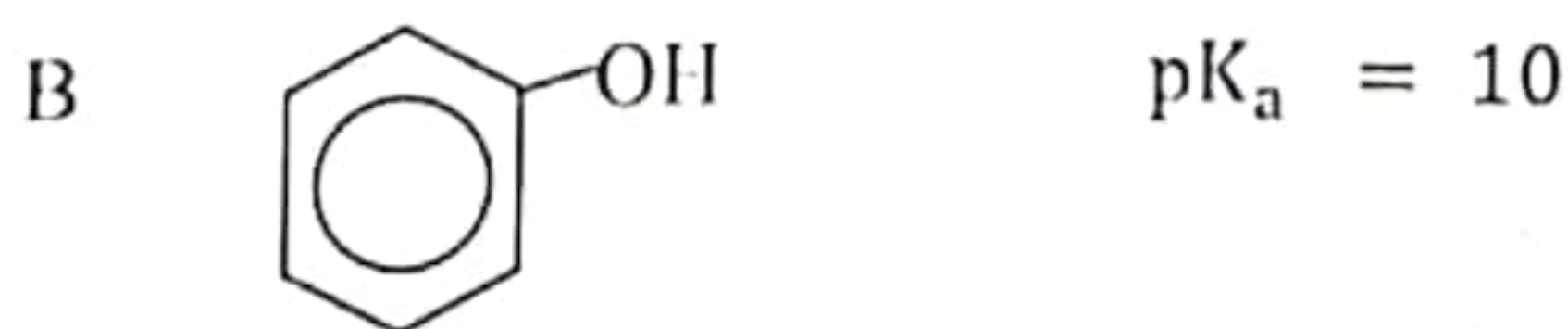
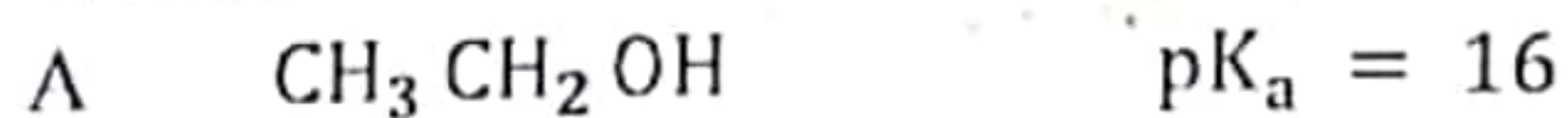
Question 93

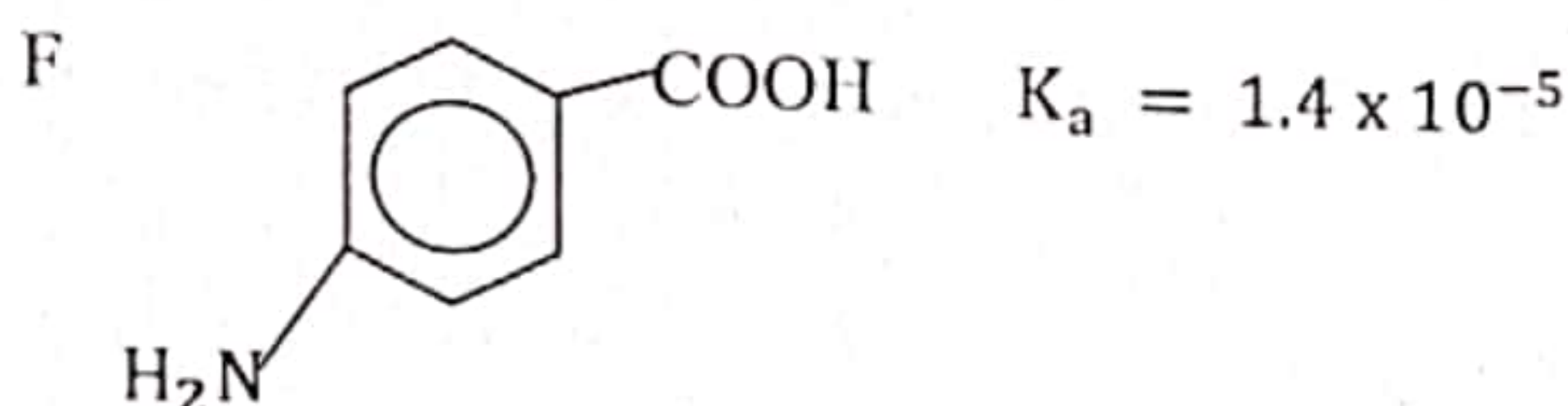
- a) Compare acidities of the given pairs of compounds and for each pair give reasons for the different in acidity.

i) A versus B

ii) C versus D

iii) E versus F

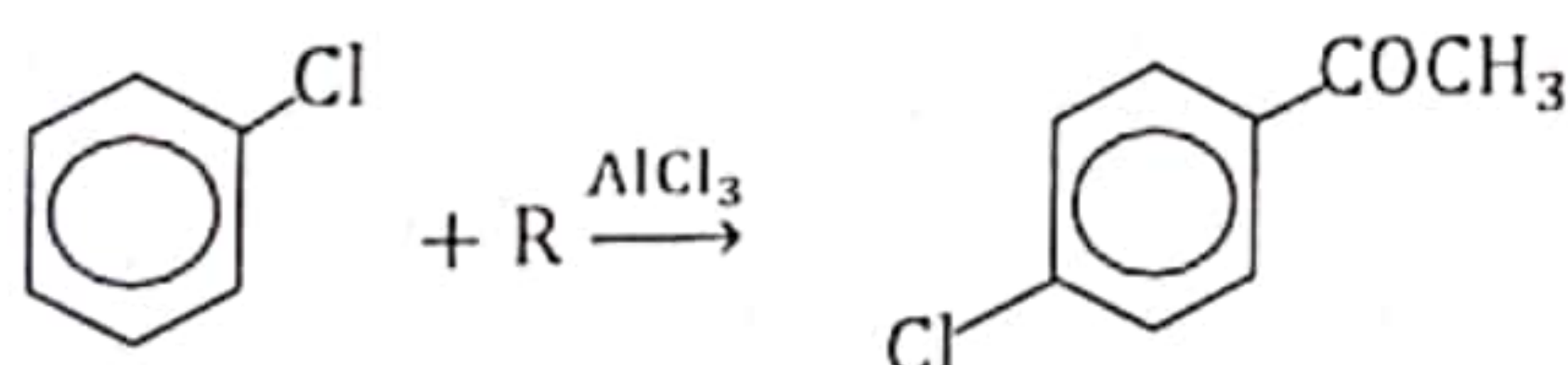




- b) Write equation to show how benzaldehyde (C_6H_5CHO) reacts with:
- Sodium hydroxide solution
 - Zinc amalgam and concentrated HCl
 - Tollen's reagent
 - Warm phenylamine
 - Acidified potassium permanganate solution

Question 94

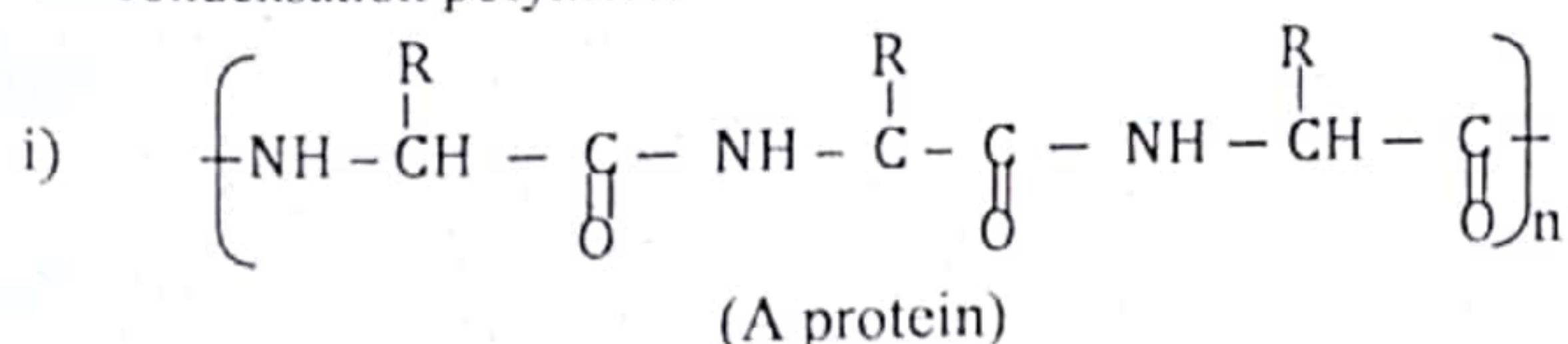
- a) Show how you would carry out the following conversions.
- CH_3OH to CH_3COONH_4
 - CH_3CH_2COOH to CH_3COOH
- b) Study the following reactions and answer the question below
- $A + \text{Ozonolysis} \rightarrow B (C_2H_4O) + Q (C_4H_8O)$

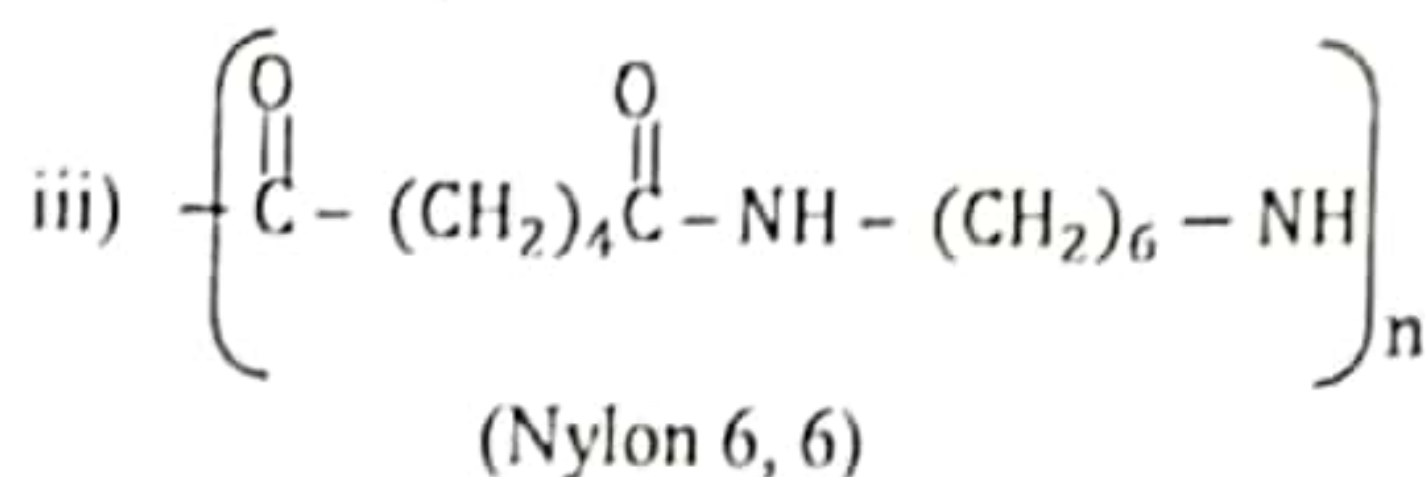
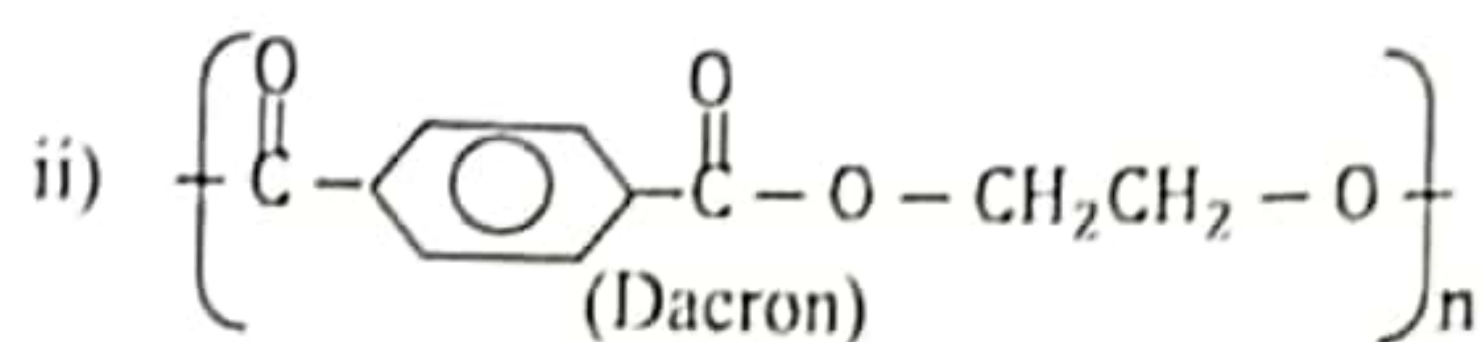


- Write the structure of the compound A, B, Q, D and
- Give the systematic (IUPAC) names of the compound A, B, Q, D and R

Question 95

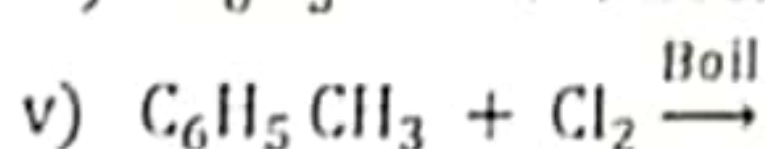
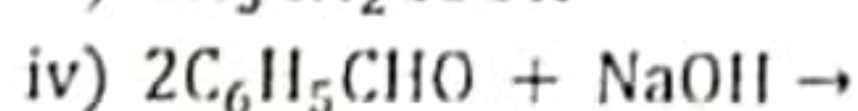
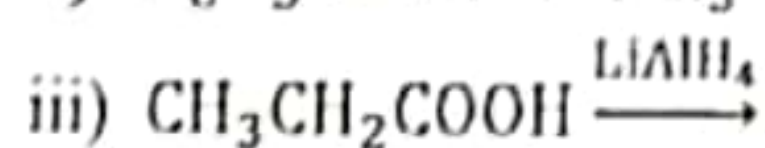
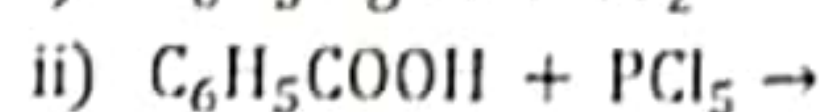
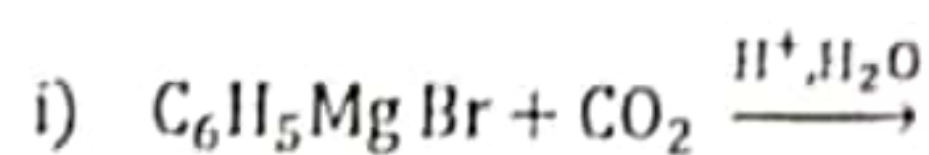
- a) Define the following terms
- Polymer
 - Addition polymerisation
 - Condensation polymerisation
- b) Name at least four common natural polymers
- c) Differentiate thermosetting polymers from thermoplastic polymers, giving example for each.
- d) Using the example of polymerisation of vinyl chloride, C_2H_3Cl to form PVC show:
- The chain initiation step.
 - The chain propagation step.
 - The chain termination step.
- e) Write the complete structures of the monomers which were used to prepare each of the following condensation polymers.





Question 96

Complete the following reactions.



Question 97

4.1g of bromoalkane was reacted with excess sodium hydroxide solution, the resulting solution was acidified with excess nitric acid and diluted to exactly 250cm^3 . 25cm^3 of this solution required 33.28cm^3 of 0.1M silver nitrate solution for complete precipitation of silver bromide.

- Calculate the relative molecular mass of bromoalkane
- From your answer to (a) above deduce the molecular formula of bromoalkane.
- Write structural formula of the possible isomers of the bromoalkane
- Explain the difference in reactivity of one of the bromoalkane you have given in (c) and bromobenzene with sodium hydroxide.

Question 98

Explain the following; the boiling point of propanoic acid is 141°C while that of 1-butanol, an alcohol of comparable molecular weight is 118°C .

Question 99

Why chloroform is kept in dark bottles?

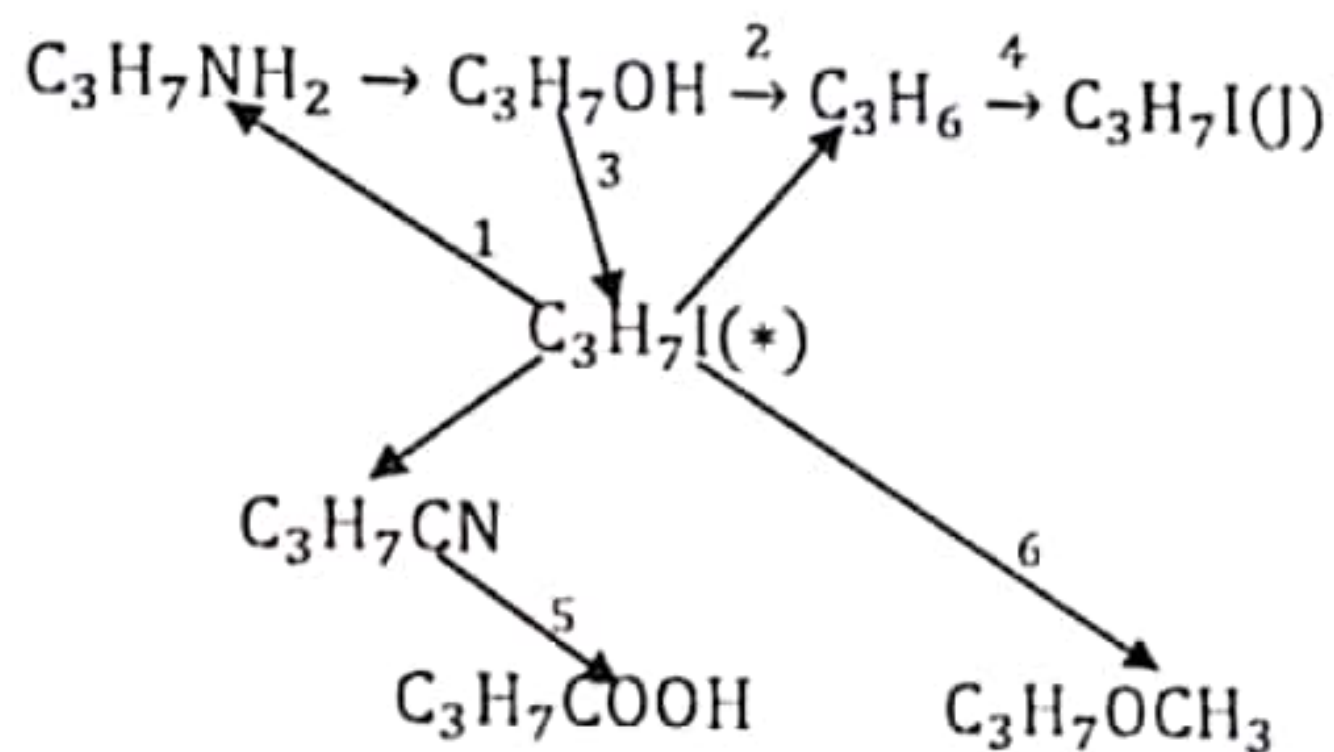
Question 100

Why iodoform gives precipitate with silver nitrate on heating while chloroform does not?

Question 101

The diagram below sets out some single step reactions of an iodopropane C_3H_7I (*) and some related compounds.

- a) Give the names of formula of the reagent(s) and (i) an approximate indication of the temperature used (ii) the name (or formula) of any solvent, for each of the step 1 to 6.
- b) The formula (C_3H_7I) appear twice in the reaction scheme, marked by an asterisk (*) and a letter (J) but does not refer to the same compound. Write to the full structures of these compounds.



SOLUTIONS TO EXAMINATION QUESTIONS

EXAMINATION QUESTIONS-1

Question 1

- (i) Lone pair on N of phenyl amine are less available for the donation to Lewis acid due to their delocalisation in the mesomerism.
 (ii) Lone pair on N of ethanamide are less available for the donation to Lewis acid due to negative inductive effect exerted by O and delocalisation of the lone pair in the mesomerism.

Question 2

Lone pair on N of ethyl amine are more available for the donation to Lewis acid due to positive inductive effect exerted by ethyl group.

Question 3

- (i) To satisfy market demand for:
 1. Smaller hydrocarbons 2. Alkenes 3. Alkynes
- (ii) $C_{14}H_{30} \rightarrow C_2H_4 + C_{12}H_{26}$ (Another possible equation is $C_{14}H_{30} \rightarrow C_3H_6 + C_{11}H_{24}$)

Question 4

- (a) (i) Free radical substitution
- (ii) UV light (sunlight) or high temperature (150°C to 500°C)
- (iii) Propagation
- (iv) Termination
 $CH_3CH_2^{\bullet} + Br^{\bullet} \rightarrow CH_3CH_2Br$
 $CH_3CH_2^{\bullet} + CH_3CH_2^{\bullet} \rightarrow CH_3CH_2CH_2CH_3$

Question 5

- (a) (i) $CH_3CH_3 + Cl_2 \xrightarrow{\text{UV light}} CH_3CH_2Cl + HCl$
 (ii) In the termination step, two ethyl radicals may collide to give butane according to the following equation:
 $CH_3CH_2^{\bullet} + CH_3CH_2^{\bullet} \rightarrow CH_3CH_2CH_2CH_3$
- (b) (i) $CH_2 = CH_2 + Cl_2 \xrightarrow{\text{CCl}_4, \text{darkness, low temperature}} CH_2ClCH_2Cl$
 (ii) All carbons in ethane are sp^3 hybridised thus making it saturated and hence chlorination in ethane is substitution reaction. Carbons in ethene are sp^2 hybridised thus making it unsaturated and hence chlorination in ethene is addition reaction. Also ethene reacts with electrophile in electrophilic addition because it has reactive pi electrons which are capable of polarizing chlorine molecule thus forming electrophile while ethane having all of its bond sigma cannot polarize the chlorine molecule and therefore it reacts with free radicals (chlorine radicals) in free radical substitution reaction.
 (iii)
- It is too valuable in synthesis of other important organic compounds, e.g. in production of polymers.
 - Its combustion is inefficient due to their smaller H to C ratio.

Question 6

- (a) (i) $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
- (ii) Concentrated sulphuric acid
- (iii) NO_2^+

- (b) (i) $Cl_2 \xrightarrow{\text{UV light}} 2Cl^{\bullet}$
- (ii) $C_6H_5CH_3 + Cl^{\bullet} \rightarrow C_6H_5CH_2^{\bullet} + HCl$
 $C_6H_5CH_2^{\bullet} + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl^{\bullet}$

(No need of including curved arrows because you were asked just to 'write equations')

- (iii) $C_6H_5CHCl_2 / C_6H_5CCl_3$ (You may include any other possible product which may be formed in the termination step like $C_6H_5CH_2CH_2C_6H_5$)

(a)

Type of reaction: nitration or electrophilic substitution

Reagent(s): $\text{HNO}_3 + \text{H}_2\text{SO}_4$

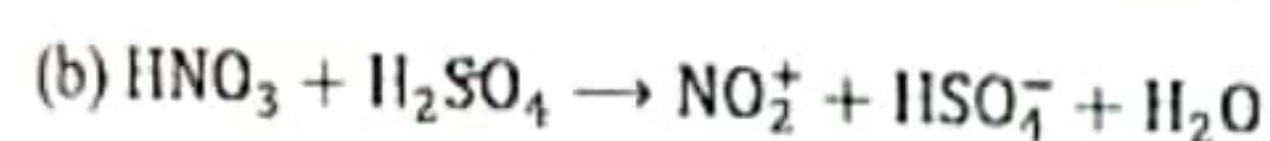
Type of reaction: sulphonation or electrophilic substitution

Reagent(s): $\text{SO}_3 + \text{H}_2\text{SO}_4$

Type of reaction: reduction or amination or hydrogenation

Reagent(s): HCl | Fe or Sn or Zn or Zn or SnCl_2 in place of Fe . Other possible answers are:

- H_2 | Ni or Pt or Pd in place of Ni
- $LiAlH_4$



(i) In the production of poly(phenylethene) or polystyrene.

(ii) $\text{CH}_3\text{CH}_2^+; \text{CH}_2 = \text{CH}_2 + \text{HCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CH}_2^+ + \text{AlCl}_4^-$
} Forms $\text{CH}_3\text{CH}_2\text{Cl}$

(iii) Elimination or dehydrogenation

(iii) $\text{CH}_3\text{CH}_2\text{Cl}$
Elimination or dehydrogenation

The enthalpy of hydrogenation is not expected one ($3 \times -120 = 360 \text{ kJ mol}^{-1}$) because π bonds in benzene are stabilised by delocalisation in the mesomerism and hence extra energy called resonance energy amounted to 152 kJ mol^{-1} is absorbed to break the resonance before doing addition of hydrogen atoms.

Cl is electron withdrawing by negative inductive effect, and it electron releasing by positive mesomeric effect. When electrophile substitute at ortho and para position of chlorobenzene, the intermediate carbenium ion becomes more stable because when there is positive charge at carbon adjacent to chlorine, the positive mesomeric effect of Cl outweighs negative inductive effect and therefore its lone pairs in participate in the stabilisation of the positive charge.

In case of halogenations of benzene Br_2 is polarised by FeBr_3 , but in case of phenol the polarization of Br_2 takes place by phenol due to highly activating effect (by positive mesomerism) of OH group present on the benzene ring.

OH group present on the phenol is electron releasing and activates the benzene ring through positive mesomerism.

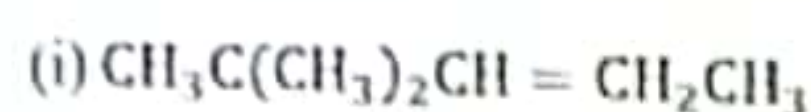
Sulphuric acid is helping in formation of NO_2^+ electrophile which is easy to substitute on benzene.

As branching increases, positive inductive effect increases; this decreases acidity.

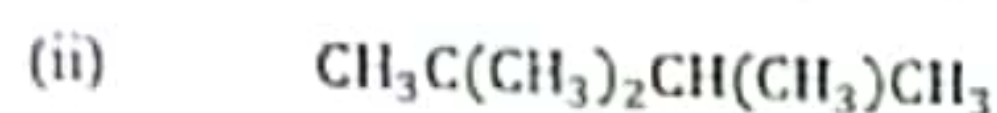
Basic strength of amines depends not only depends on electron releasing effect through +I but also steric effect. So secondary amine is stronger base than primary amine because has stronger positive effect while primary amine is stronger base than tertiary amine because has weaker steric hindrance. Hence the given order of basic strength is correct.

Nitration takes place in the presence of H^+ ions (concentrated sulphuric acid as catalyst) which protonates on amine (which is basic) and forms H_3N^+ in anilinium ion ($C_6H_5NH_3^+$) which behaves as electron withdrawing group, hence it forms some amount of meta product.

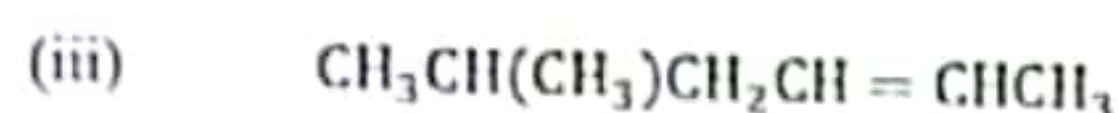
Question 17



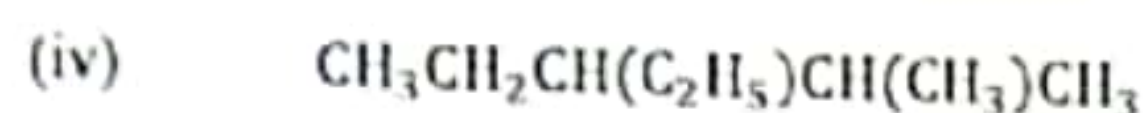
Correct IUPAC name: 4,4-dimethyl-2-pentene.



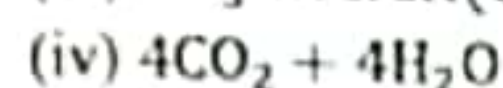
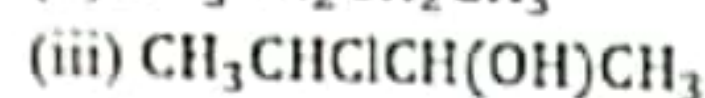
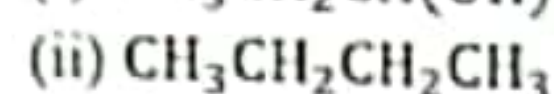
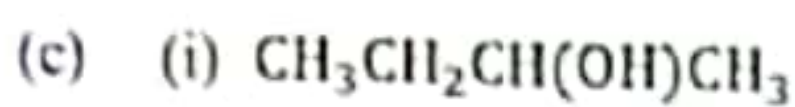
Correct IUPAC name: 2,2,3-trimethylbutane.



Correct IUPAC name: 5-methyl-2-hexene.



Correct IUPAC name: 3-ethyl-2-methylpentane.



Question 18

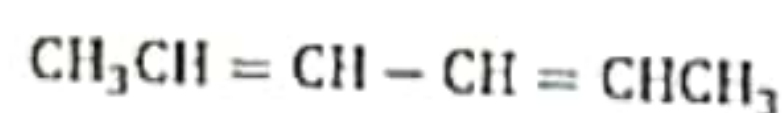
pK_b value of CH_3NH_2 is lower than that NH_3 implying that the amine is stronger base because the methyl group in it release electrons to the nitrogen by positive inductive effect thus making it more basic.

Question 19

- The molecular formula of compound E which is C_6H_{10} confirms general molecular formula of $\text{C}_n\text{H}_{2n-2}$.
- Thus compound E may be aliphatic alkyne with only one carbon-carbon triple bond, aliphatic diene or cycloalkene with only one C = C.

Product formed after bromination indicate that 2 moles of Br_2 were added.

- Thus compound E cannot be cycloalkene with only one C = C, it may be aliphatic alkyne with one carbon-carbon triple bond or aliphatic diene.
- Treatment of compound E with $\text{Cu}(\text{NH}_3)_2\text{OH}$ confirms that compound E is aliphatic alkyne with no terminal triple bond or aliphatic diene.
- Product formed on ozonolysis confirms that compound E can not be alkyne (alkyne would give carboxylic acids and not carbonyl compounds), it must be aliphatic diene with the following structure:



Question 20

- Reactions of compound A indicate that it must be a saturated hydrocarbon that is alkane.
- Reactions of compound B indicates that it must be an unsaturated hydrocarbon that is either alkene or alkyne with no terminal carbon-carbon triple bond.
- Reaction of compound C indicates that it must be an alkyne with carbon-carbon terminal triple bond.
- Product formed on combustion confirms that there is three atoms of carbon in each of compound A, B and C since three moles of CO_2 were produced.
- Since there is no alkyne with three carbon atoms without carbon-carbon terminal triple bond, B is must be alkene.

Hence structure of A is $\text{CH}_3\text{CH}_2\text{CH}_3$

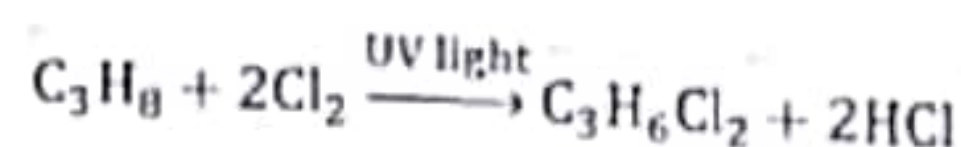
Structure of B is $\text{CH}_3\text{CH}=\text{CH}_2$

Structure of C is $\text{CH}_3\text{C}\equiv\text{CH}$

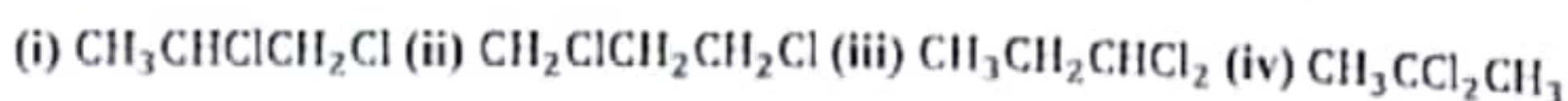
Refer to the texts for solution of part (b) and (c)

Question 21

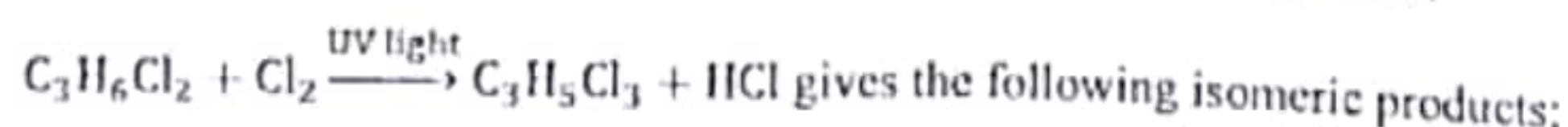
- Propane undergoes dichlorination according to the equation;



Possible isomers of the organic product are;



- Further chlorination of above compounds is according to the equation;



(i) Gives the following products:

(a) $\text{CH}_3\text{CHClCHCl}_2$ (b) $\text{CH}_3\text{CCl}_2\text{CH}_2\text{Cl}$ (c) $\text{CH}_2\text{ClCHClCH}_2\text{Cl}$

Thus (i) gives three chloro compounds and hence it can be either be A or B

(ii) Gives the following products:

(a) $\text{CH}_2\text{ClCH}_2\text{CHCl}_2$ (b) $\text{CH}_2\text{ClCHClCH}_2\text{Cl}$

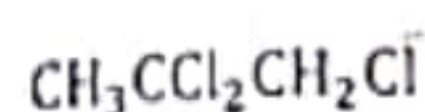
Thus (ii) gives the two chloro compounds and hence it must be D.

(iii) Gives the following products:

(a) $\text{CH}_3\text{CH}_2\text{CCl}_3$ (b) $\text{CH}_3\text{CHClCHCl}_2$ (c) $\text{CH}_2\text{ClCH}_2\text{CHCl}_2$

Thus (iii) gives three chloro compounds and hence it can either be A or B

(iv) gives the following product,



Thus (iv) gives only one product, hence it must be C

So structure of C is $\text{CH}_3\text{CCl}_2\text{CH}_3$

And structure of D is $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{Cl}$

Trichloropropane from C is identical to that of (b) from (i) and hence structure of A is (i).

Therefore structure A is $\text{CH}_3\text{CHClCH}_2\text{Cl}$

And that of B is (iii) that is $\text{CH}_3\text{CH}_2\text{CHCl}_2$

Question 22

Mass of C in 44g of CO_2 is 12g

So mass of C in 1.173g of CO_2 will be $\frac{1.173 \times 12}{44}$ g

% of C in the compound is $\frac{1.173 \times 12}{44 \times 1.1} \times 100\% = 29.08\%$

Mass of H in 18g of H_2O is 2g

So mass of H in 0.24g of H_2O will be $\frac{0.24 \times 2}{18}$ g

% of H in the compound is $\frac{0.24 \times 2}{18 \times 1.1} \times 100\% = 2.42\%$

Thus % of O = $100 - (2.42 + 29.08) = 68.5\%$

Constituent atoms in the compound	C	H	O
% of each	29.08	2.42	68.5
Mass of each in 100g of the compound	29.08g	2.42g	68.5g
Number of moles of each; $n = \frac{m}{M_r}$	$\frac{29.08\text{g}}{12\text{g mol}^{-1}} = 2.42\text{mol}$	$\frac{2.42\text{g}}{1\text{g mol}^{-1}} = 2.42\text{mol}$	$\frac{68.5\text{g}}{16\text{g mol}^{-1}} = 4.28\text{mol}$
Divide by the smallest to get simpler ratio	$\frac{2.42\text{mol}}{2.42\text{mol}} = 1$	$\frac{2.42\text{mol}}{2.42\text{mol}} = 1$	$\frac{4.28\text{mol}}{2.42\text{mol}} = 2$

Hence empirical formula of the compound is CHO_2

Using $T = K_f m = \frac{K_f \times m_s}{M_s \times m_v \text{ in kg}}$

From which $M_s = \frac{K_f \times m_s}{T \times m_v \text{ in kg}} = \frac{1.86 \times 1.12}{0.186 \times 0.025} \text{ g mol}^{-1} = 448 \text{ g mol}^{-1}$

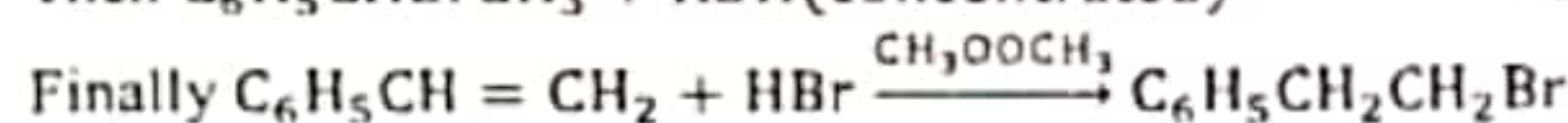
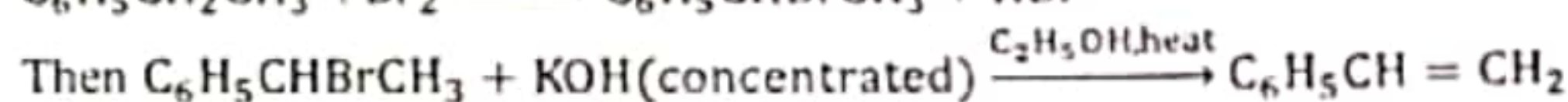
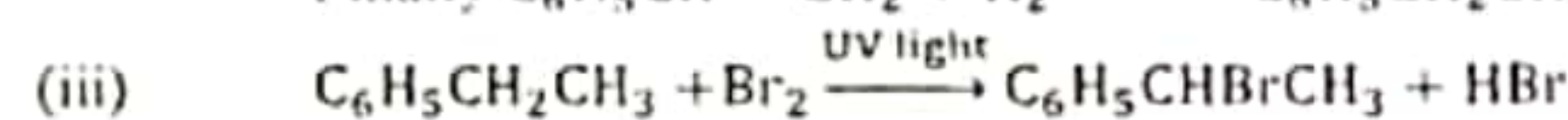
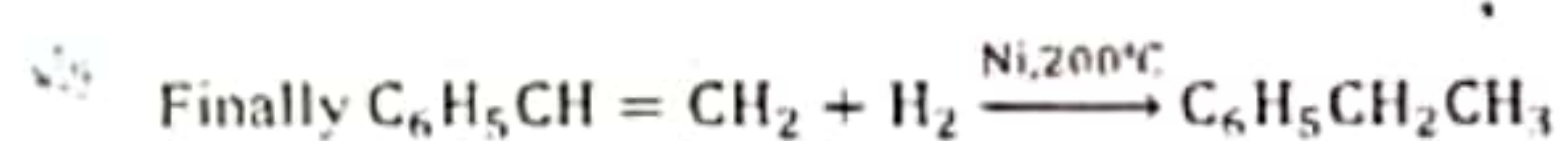
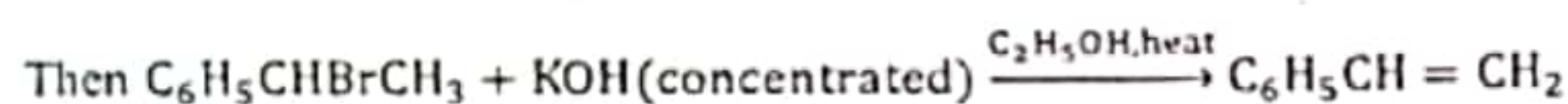
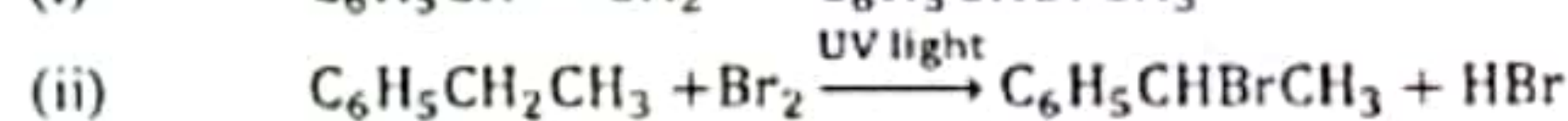
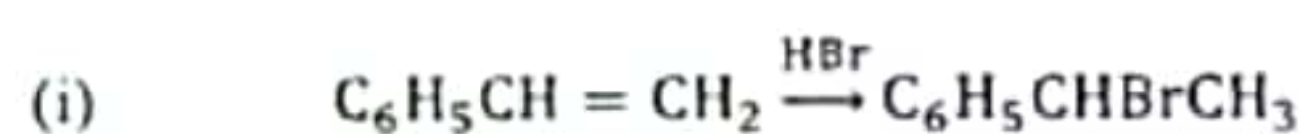
Let molecular formula be $(\text{CHO}_2)_n$

$$\text{Then } 12n + n + 32n = 448; 45n = 448$$

From which $n = 10$ (correct to nearest whole number)

Hence molecular formula of the compound is $C_{10}H_{10}O_{20}$

Question 23



Question 24

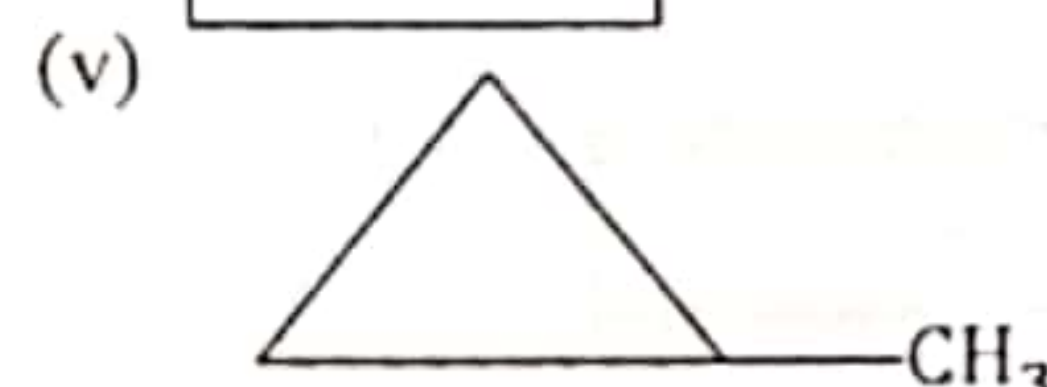
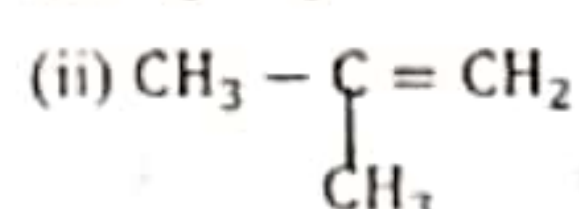
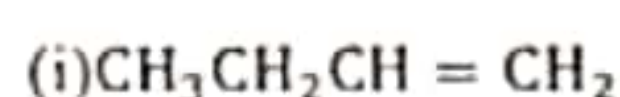
(iii) Because HI has lower boiling point (399K) at 1atm (atmospheric pressure). So in presence of the large pressure, its boiling point is raised and it become above 399K as well as above 420K (the temperature at which the reaction takes place) and hence handling of material become easier.

(iv) To prevent occurrence of reverse reaction by combining with liberated iodine which would react with alkane to form reverse reaction. $2P + 3I_2 \rightarrow 2PI_3$

- Hydrogenation of unsaturated side chain of benzene requires lower temperature than that required for hydrogenation in benzene ring. At high temperature hydrogenation occurs in both side chain and benzene ring.

Question 25

(a) Isomers of Y are:



(b) Since Y gives only one product on ozonolysis, it must be symmetrical alkene

- But among mentioned isomer, symmetrical alkene is (iii) only.

- Hence Y is but-2-ene with the following structure: $CH_3CH=CHCH_3$

Ozonolysis of but-2-ene followed by hydrolysis (in absence of zinc) gives ethanoic acid with the following structure:



Note:

Absence of zinc made the product to be carboxylic acid. In its presence the product become aldehyde (CH_3CHO)

Question 26

CaC_2 reacts with H_2O to give ethyne according to the following equation: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$

From which mole ratio of CaC_2 to C_2H_2 is 1:1

$$\text{From } PV = nRT \quad \text{or } n = \frac{PV}{RT}$$

Thus number of moles of C_2H_2 (ethyne) formed was;

$$n = \frac{1 \times 200 \times 10^{-3}}{0.082 \times 300} = 8.13 \times 10^{-3} \text{ mol}$$

From the mole ratio: number of moles of CaC_2 was also $8 \times 10^{-3} \text{ mol}$

But molar mass of $CaC_2 = 64 \text{ g/mol}$

Whence mass of $\text{CaC}_2 = 8 \times 10^{-3} \times 64\text{g} = 0.52\text{g}$ of CaC_2 in 0.64g of its impure form

$$\text{Then } \% \text{CaC}_2 = \frac{0.52}{0.64} \times 100\% = 81.25\%$$

Hence the percentage purity of calcium carbide is 81.25%

Question 27

$$\text{Number of moles of carbon atoms} = \frac{7.2\text{g}}{12\text{g mol}^{-1}} = 0.6\text{mol}$$

$$\text{Number of moles of hydrogen atoms} = \frac{1.2\text{g}}{1\text{g mol}^{-1}} = 1.2\text{mol}$$

$$\text{Number of moles of oxygen atoms} = \frac{9.6\text{g}}{16\text{g mol}^{-1}} = 0.6\text{mol}$$

Thus C: H: O = 0.6: 1.2: 0.6

Then dividing by smallest to get the simpler ratio; $\frac{0.6}{0.6} : \frac{1.2}{0.6} : \frac{0.6}{0.6} = 1: 2: 1$

Hence the empirical formula of the compound is CH_2O

Let the molecular formula of the compound be $(\text{CH}_2\text{O})_n$

$$\text{Then } 12n + 2n + 16n = M_r = 180 \text{ or } n = 6$$

Hence molecular formula of the compound is $\text{C}_6\text{H}_{12}\text{O}_6$

(Alternatively you can find percentage by mass of each constituent element and then you may continue).

Question 28

(a) Aromatic (b) Ester (c) Alcohol (d) Alkyne (e) Alkane (f) Ether (g) Aldehyde (h) Ketone (i) Carboxylic acid (j) Alkene

Question 29

- (i) 3,6-dimethylheptane
- (ii) 2,3,7-trichloro-5-ethyloctane
- (iii) 2-ethylpent-1-ene
- (iv) 4,4-dichloropent-2-yne
- (v) Trans-hex-2-ene
- (vi) 3-chloro-2-methyl-4-phenylpent-2-ene (benzene is treated as the substituent when is attached to the more complex chain like in this case)

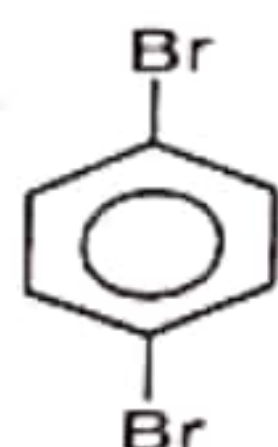
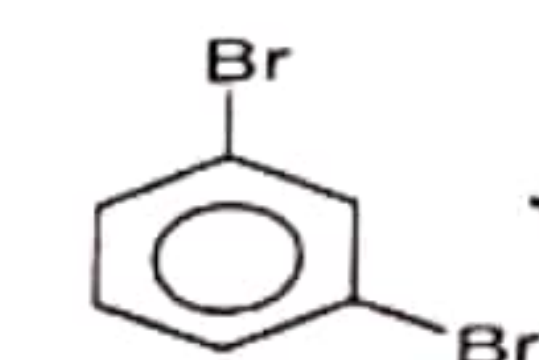
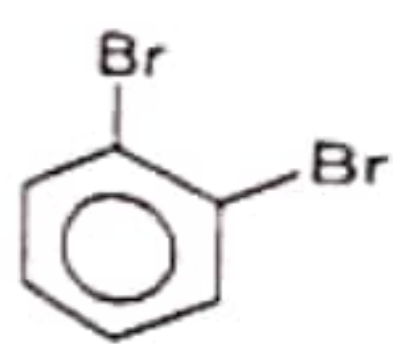
Question 30

It is direct from the text. Just apply Markownikoff's rule.

Question 31

This question is about isomers of compounds of benzene. In (a), you could use the number-based nomenclature, or the ortho, meta, para style shown below:

(a)

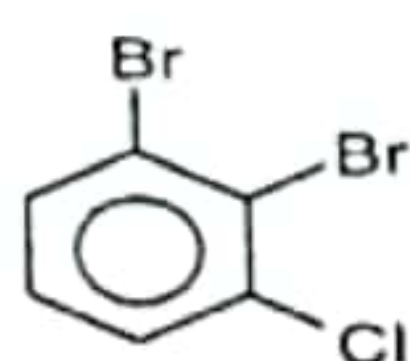


o-dibromobenzene

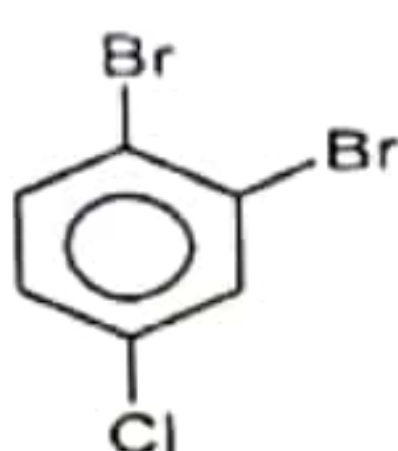
m-dibromobenzene

p-dibromobenzene

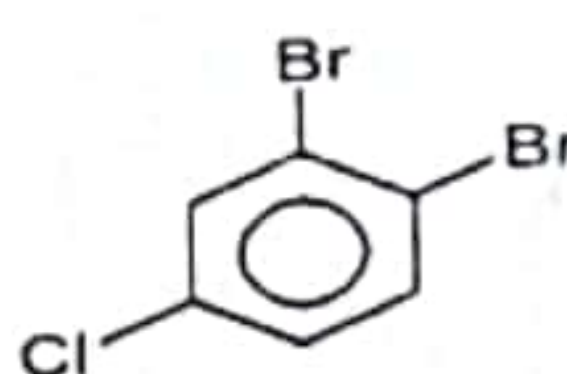
(b)



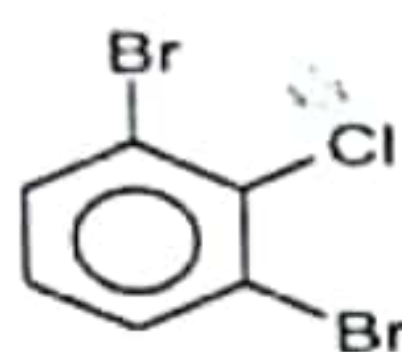
1,2-dibromo-3-chlorobenzene



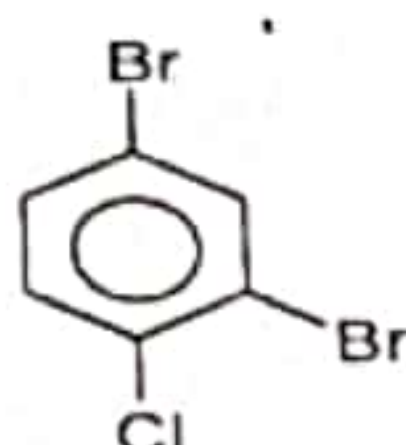
1,2-dibromo-4-chlorobenzene



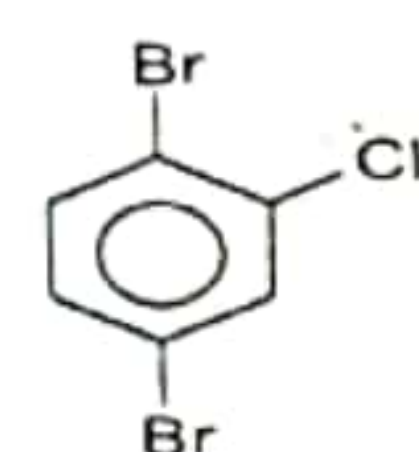
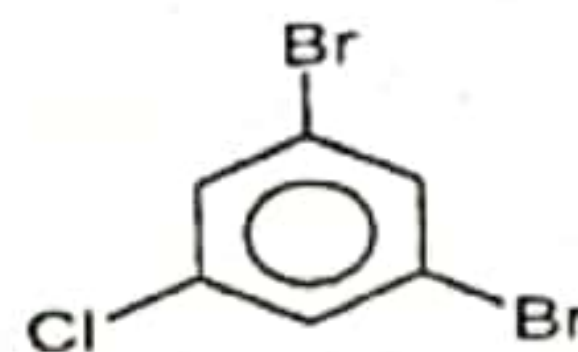
1,3-dibromo-5-chlorobenzene



1,3-dibromo-2-chlorobenzene



1,3-dibromo-4-chlorobenzene



1,4-dibromo-2-chlorobenzene

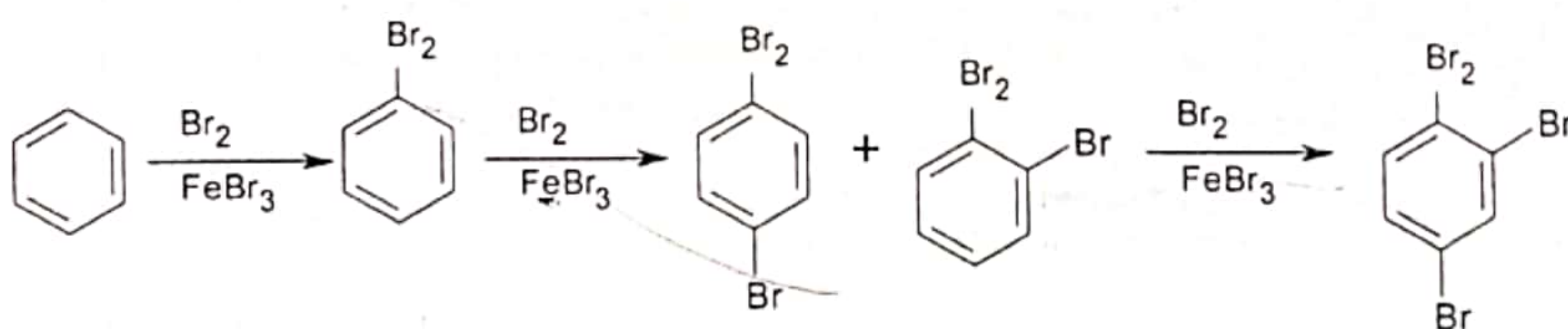
Question 32

Hints to the solution of Question 32.

- hydrogen gas, palladium catalyst, mild conditions
The ring is stable to these conditions (much more vigorous treatment is required to reduce it via addition reaction), so no reaction occurs.
- hot potassium permanganate
The ring is stable to this oxidation, but the side chain will react. The product will be benzoic acid
- nitric and sulphuric acid
The alkyl substituent is an o,p-director, so we will get o-nitropropylbenzene and p-nitropropylbenzene with the para product as the major product due to steric hindrance.
- bromine, heat and light
The ring is stable to free radical conditions, but the side chain bromination at the benzylic position to yield 1-bromo-1-phenylpropane occurs.
- bromine and aluminum chloride
Here the reaction at the o- and p-positions to give o-bromopropylbenzene and (mostly) p-bromopropylbenzene.

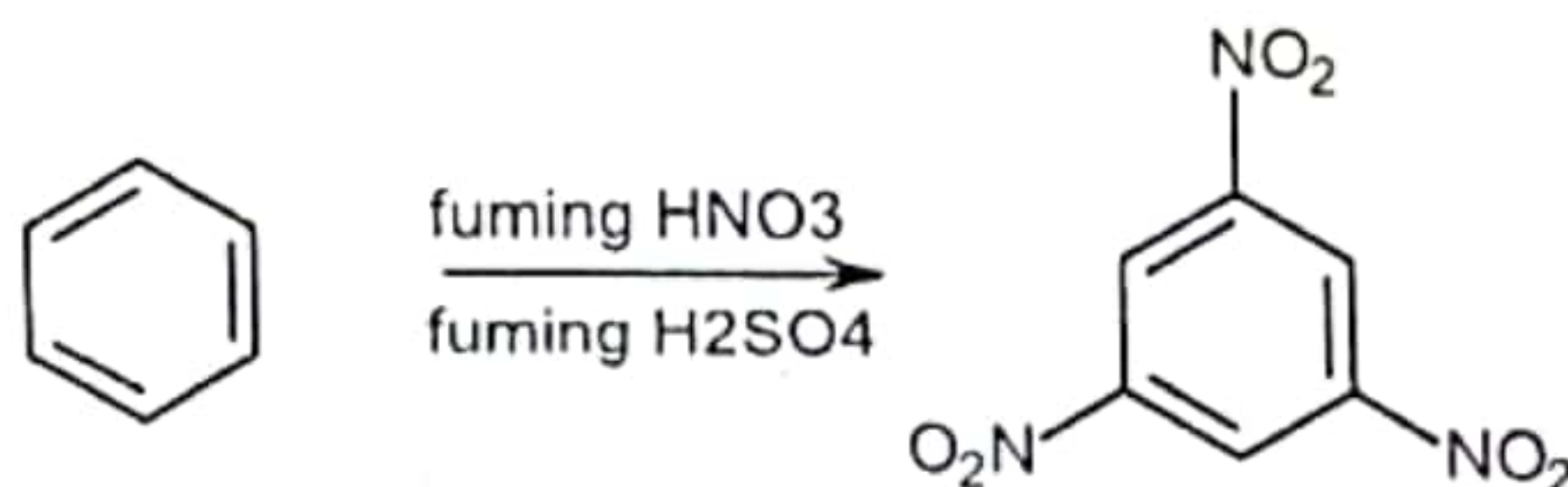
Question 33

(a)



(b)

Here the fact that the nitro group is a deactivator means that we just have to use very vigorous conditions to tri-nitrate the ring. Using fuming nitric and sulphuric acid should do the trick: The nitric acid should be in excess.

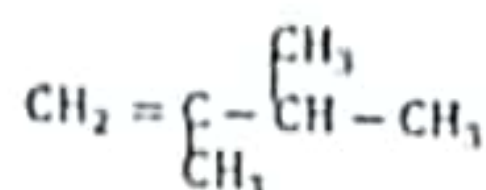


(You may show the reaction in steps like in (a) above)

EXAMINATION QUESTIONS-2

Question 1

- a)
- 2,3-dimethylbutan-2-ol
 - Elimination reaction
 - Structure



Explanations:

Loss of hydrogen atom from the terminal carbon is also possible

- b)
- $$(\text{CH}_3)_2 - \underset{\text{OH}}{\underset{|}{\text{C}}} - \text{CH}(\text{CH}_3)_2 + \text{CH}_3\text{COCl} \rightarrow (\text{CH}_3)_2\overset{\text{OCCH}_3}{\underset{|}{\text{C}}} - \text{CH}(\text{CH}_3)_2 + \text{HCl}$$
 - Type of reaction: Esterification
Reagent: CH_3COOH (ethanoic acid)
Conditions: Strong acid catalyst like H_2SO_4 or HCl

Question 2

- a)
- Propyl methanoate
 - Reagent: NaHCO_3
Observation: With NaHCO_3 , D gives effervescence of colourless gas (CO_2) while C does not indicating no reaction.
Other tests:

- Reagent: Acidified $\text{K}_2\text{Cr}_2\text{O}_7$
Observation: C change orange colouration of $\text{K}_2\text{Cr}_2\text{O}_7$ to green which D gives no change.
- Reagent: Acidified KMnO_4
Observation: C changes purple colouration of KMnO_4 to colourless while D gives no change.
- Reagent: Strong electropositive metal like sodium (Na)
Observation: D gives bubble of hydrogen gas with sodium metal while C does not.
- Reagent: litmus paper
Observation: D turns blue litmus paper red while C does not give any change to litmus.
- Reagent: Phosphorous pentachloride (PCl_5)
Observation: D gives white fumes of HCl with PCl_5 while C does not.

- b)
- Pentan - 2 - one (or 2 - pentanone)
 - Reagent: Tollen's reagent
Observation: F gives silver mirror with Tollen's reagent while E does not indicating no reaction.
Other tests:
- Reagent: Fehling's solution (or Benedict solution)
Observation: F gives brick-red precipitate with Fehling's or Benedict's solution while E does not
 - Reagent: mixture of I_2 and NaOH
Observation: E gives yellow precipitate with I_2/NaOH mixture while F does not.
 - Reagent: Acidified $\text{K}_2\text{Cr}_2\text{O}_7$
Observation: F changes orange colouration of $\text{K}_2\text{Cr}_2\text{O}_7$ while E does not.
 - Reagent: Acidified KMnO_4
Observation: F change purple colouration of acidified KMnO_4 to colourless while E does not.

Question 3

- a)
- B is propanoyl chloride
C is propanoic acid anhydride
 - White fumes of HCl would be observed
 - $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{CH}_2\text{COOH}$

- b)
- Name of alcohol: methanol
D: Methyl propanoate
 - Conditions for A:

- Presence of strong acid like H_2SO_4 and HCl
- Heat (or Reflux)

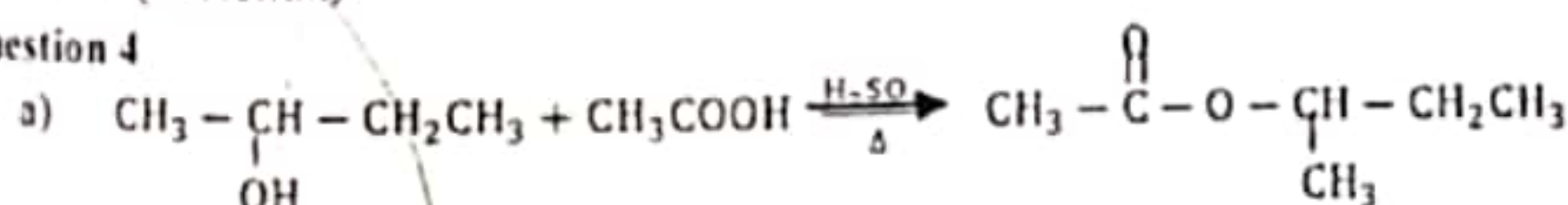
Conditions for B:

- Room temperature

Conditions for C:

- Heat (or Reflux)

Question 4



- b) Ester (Warning! Don't give the name of the organic compound! you are required to name the type of the organic compound)

Uses:

- Solvent
 - Soap making
 - Flavourings and others as discussed in the text
 - (iii) Catalyst: sulphuric acid
- Meaning of homogeneous: in the same physical state.

Question 5

- a) Reagent: NaBH_4 (or LiAlH_4)
Type of reaction: reduction
- b)
- (i) Reagents: $\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$ (or $\text{KMnO}_4, \text{H}_2\text{SO}_4$)
Conditions: reflux
 - (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O}$
- c) Reagents: HCN (or HCl/NaCN mixture)
Name of mechanism: nucleophilic addition reaction mechanism

Question 6

- a) Structure:
- $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{CH}_3 \\ | \\ \text{OH} \end{array}$$
- Name: 2-methylbutan-2-ol
- b) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- c) Elimination reaction (or more specific dehydration reaction)
- d) There is no removable H atom(s) on carbon atom adjacent to carbon with OH group.

Question 7

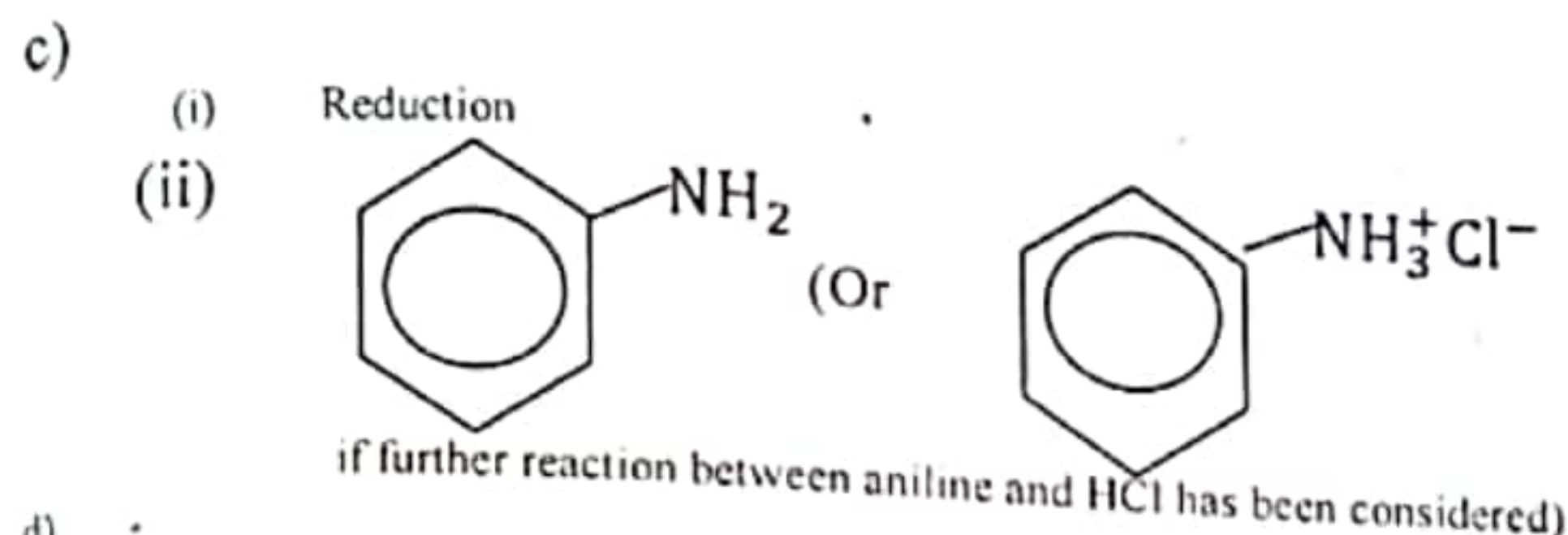
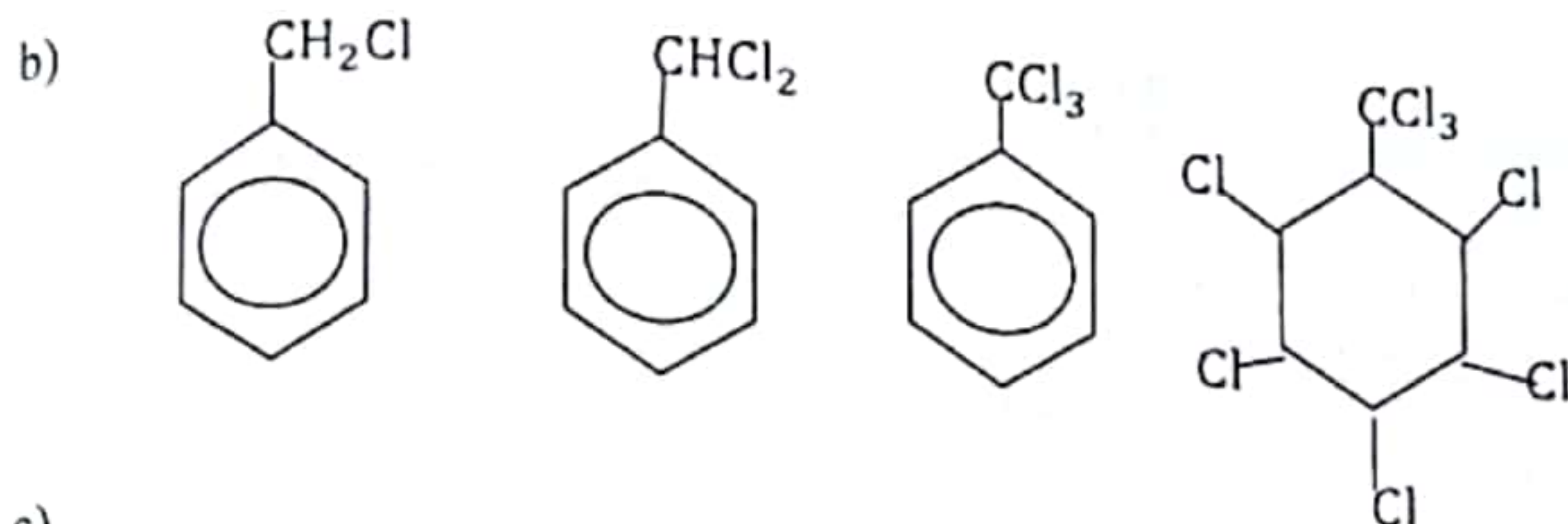
- a)
- (i) Reagent: CH_3COCl (or $(\text{CH}_3\text{CO})_2\text{O}$)
Catalyst: Anhydrous AlCl_3
 - (ii) Reduction
 - (iii) NaBH_4 (or LiAlH_4)
 - (iv) Elimination (or dehydration)
Reagent: concentrated H_2SO_4 (or H_3PO_4 or hot Al_2O_3)
- b)
- (i) In making poly(phenylethene) or polystyrene which is very useful addition polymer
 - (ii) CH_3CH_2^+
Equation: $\text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CH}_2^+ + [\text{AlCl}_4]^-$
 - (iii) Elimination (or more specific, dehydrogenation)

Question 8

- a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{NH}_3 \xrightarrow{\Delta} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HBr}$
1-bromobutane butylamine
- b)
- Step 1: $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{KCN} \xrightarrow[\text{Reflux}]{\text{CH}_3\text{CH}_2\text{OH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{KBr}$
- Step 2: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
- c)
- (i) Butyl (or alkyl) group in butyl amine exerts positive inductive effect which increases basic strength of the amine.
 - (ii) Any amine salt of strong acid like $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{Cl}$ (or small amount of hydrochloric acid)

Question 9

- a)
- (i) Reagents: chloromethane (or any other halomethane), AlCl_3 catalyst (or Fe or FeCl_3)
Conditions: anhydrous, room temperature
 - (ii) Electrophilic substitution reaction mechanism



- d)
- (i) Structure: $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
Type of reaction: Reduction
(Note: sodium tetrahydridoborate (III) is NaBH_4 , which is reducing agent)
- (ii) Structure: $\text{CH}_3 - \text{CH}_2 - \text{C}(=\text{O}) - \text{OH}$
Type of reaction: Oxidation
- (iii) Structure: $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CN}$
Type of reaction: Nucleophilic addition

Question 10

- a)
- (i) Concentrated HNO_3 /Concentrated H_2SO_4 mixture
Equation: $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$
- (ii) Name of mechanism: Electrophilic substitution reaction mechanism
Mechanism: refer to the text.
- b) Type of reaction: Reduction
Reagent: NaBH_4 (or LiAlH_4)
- c) Reagent: CH_3COCl (or $(\text{CH}_3\text{CO})_2\text{O}$)
- d) Type of reaction: Reduction
Reagents: Fe/HCl (or Sn/HCl or Zn/HCl or SnCl_2/HCl or LiAlH_4)

Question 11

- a)
- (i) Equation: $\text{C}_6\text{H}_5\text{CH}_2\text{Br} + \text{NH}_3 \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{HBr}$
(Or $\text{C}_6\text{H}_5\text{CH}_2\text{Br} + 2\text{NH}_3 \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Br}$)
- by considering further reaction between NH_3 and HBr)
- Type of reaction: nucleophilic substitution reaction.

Explanation:

Further substitution occurs to give a mixture of primary, secondary and tertiary amine (and of course quaternary ammonium compounds)

- (ii) Type of reaction: Reduction
Equation: $\text{C}_6\text{H}_5\text{CN} + 4[\text{H}] \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
Reagent: LiAlH_4 , dry ether
Explanation: The reaction gives only one product (No further substitution).

c) Phenylamine is weaker base: Lone pairs on nitrogen of phenylamine are less available as they are delocalized in the mesomerism

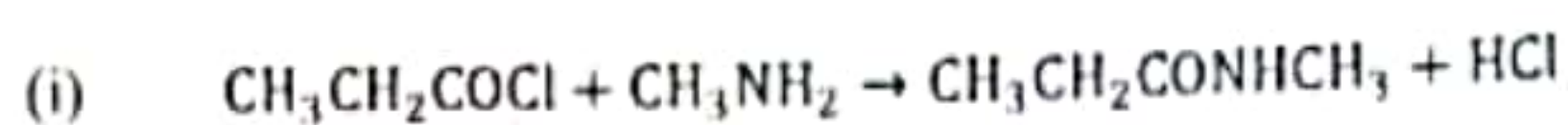
Question 12

- a)
- (i)
- (ii) Acid anhydride
- b)
- (i) ethanamine
- (ii) Reduction (or Hydrogenation)
- c) $\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CONHCH}_2\text{CH}_3 + \text{HCl}$

(Or $\text{CH}_3\text{COCl} + 2\text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CONHCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$
by considering further reaction between $\text{CH}_3\text{CH}_2\text{NH}_2$ and HCl)

Question 13

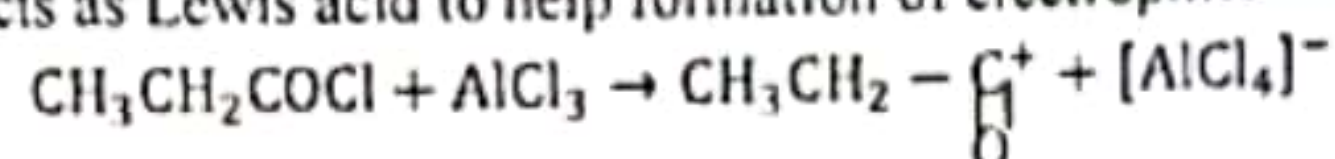
a)



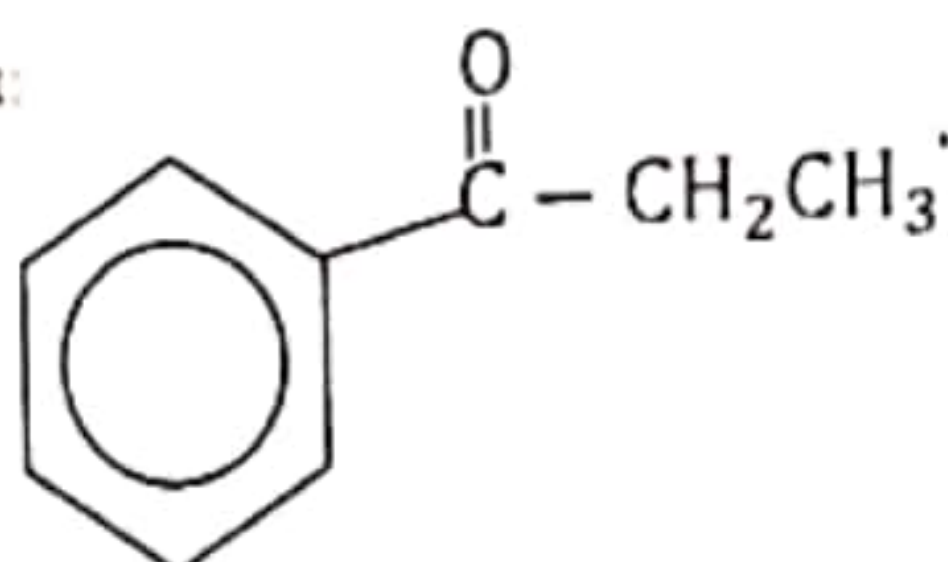
Propanoyl chloride

(ii) Condensation reaction

b) AlCl_3 acts as Lewis acid to help formation of electrophile as per equation:



Organic product:



c) Equation: $\text{CH}_3\text{CH}_2\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HCl}$

Molar mass of $\text{CH}_3\text{CH}_2\text{COCl}$ is 92.5 g/mol

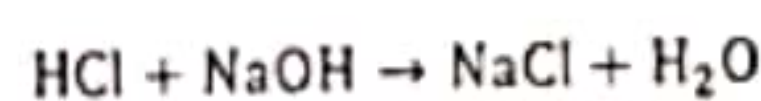
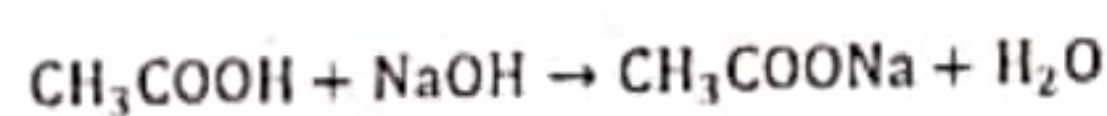
Then number of moles of $\text{CH}_3\text{CH}_2\text{COCl}$ is $\frac{1.4 \text{ g}}{92.5 \text{ g/mol}}$ using $(n = \frac{m}{M_r})$

= 0.016 mol = number of moles of CH_3COOH (Mole ratio of

CH_3COCl to CH_3COOH is 1:1)

But mole ratio of $\text{CH}_3\text{CH}_2\text{COOH}$ to HCl is 1:1

Therefore number of moles of HCl produced was also 0.016 mol. Thereafter introduction of NaOH from the burette, the alkaline solution will react with both $\text{CH}_3\text{CH}_2\text{COOH}$ and HCl present in the solution as per equations:



(Note: in presence of large amount of water, i.e. excess water, the hydrogen gas, HCl(g) will dissolve in water to give hydrochloric acid solution HCl(aq) and therefore will not escape from the container)

It follows that:

- Number of moles of NaOH react in (i) was also 0.016 mol (Mole ratio of NaOH to CH_3COOH is 1:1)
- Number of moles of NaOH reacted in (ii) was also 0.016 mol (Again mole ratio of NaOH to HCl is 1:1)
- Whence the total number of moles of NaOH required to react with mixture
= (0.016 + 0.016) mol = 0.032 mol

Then using $[] = \frac{n}{v}$ or $v = \frac{n}{[]}$

Volume Of NaOH Required = $\frac{0.032 \text{ mol}}{0.42 \text{ mol dm}^{-3}} = 0.0762 \text{ dm}^3$ or 76.2 cm^3

Hence the volume of NaOH required is 76.2 cm^3 .

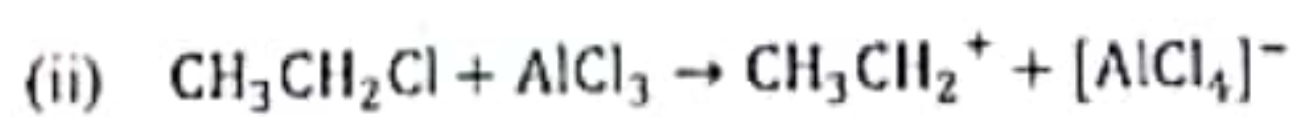
Question 14

a)

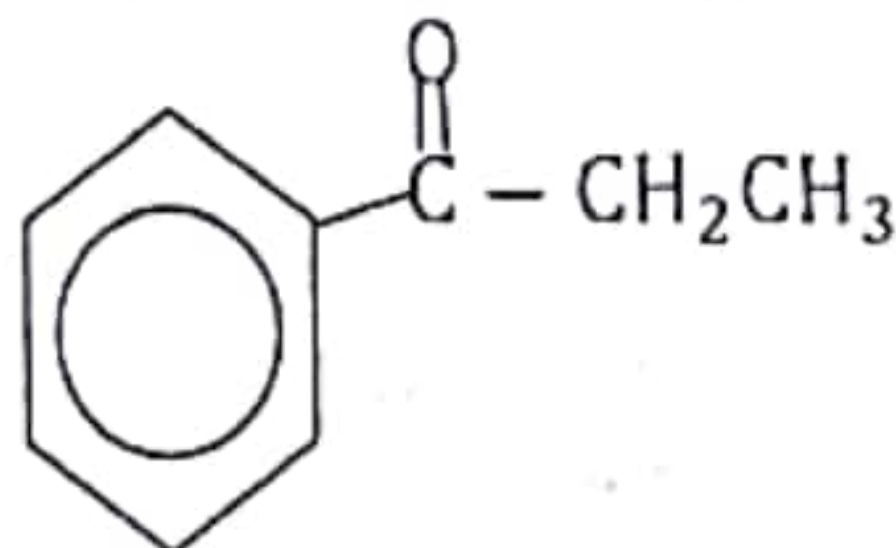
(i) Name: ethylbenzene

Reagent: $\text{CH}_3\text{CH}_2\text{Cl}$ (or $\text{CH}_2\text{CH}_2\text{Br}$)

Catalyst: AlCl_3 (or AlBr_3) or FeCl_3 (FeBr_3)



b) (i) Y is



Reagents: $\text{CH}_3\text{CH}_2\text{COCl}$ (Or $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$), AlCl_3

(ii) NaBH_4 (or LiAlH_4)

Question 15

- a)
- X is nitrile with the following structure:
 $\text{CH}_3 - \text{C} \equiv \text{N}$
 - Y is amine with the following structure:
 $\text{CH}_3 - \text{CH}_2 - \text{NH}_2$

For steps 1:

Reagents: KCN

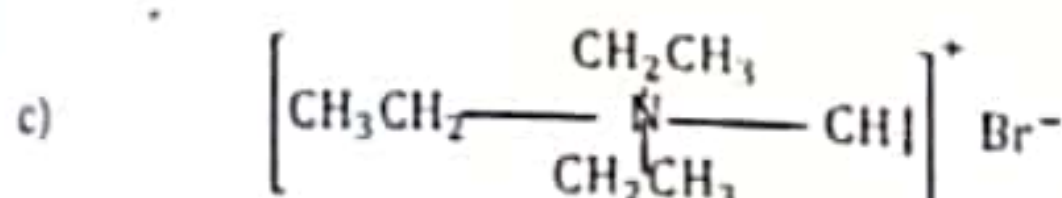
Condition: Alcohol ($\text{C}_2\text{H}_5\text{OH}$), Reflux

For step 2:

Reagents: LiAlH_4

Condition: Dry ether

- b) Secondary amine (or simply amine)



Uses:

- Surfactant
- Bactericide
- Detergent
- Fabric softener
- Hair conditioner (any two uses)

Question 16

- a) $\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{HCl}$
- b) Polymers in clothes terylene contain a ester group (Polymers in clothing are polyester) which is hydrolyzed by alkali while poly (phenylethene) is an addition polymer contain uncreative non-polar $\text{C} - \text{C}$ which is saturated.

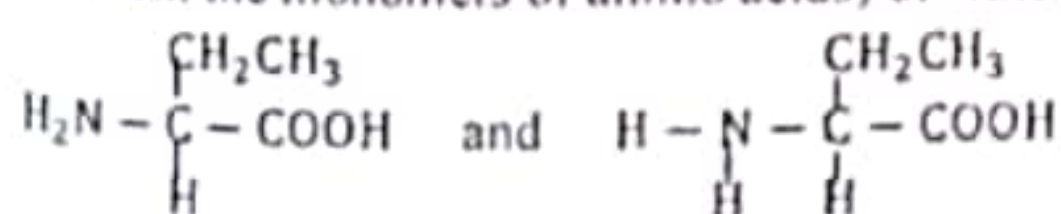
Question 17

- a) Base induced β elimination reaction
- b) Physical state varies from gas, liquid to solid
- Melting point increases
 - Boiling point increases
 - Density increases
 - Viscosity increases
- c) Addition polymerisation
- d)
- (i) $\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{OH}$
- (ii) Conditions
- Vapour phase
 - High temperature of $250^\circ\text{C} - 350^\circ\text{C}$
 - High pressure of $50\text{atm} - 70\text{atm}$
 - Strong acid catalyst like H_2SO_4 and H_3PO_4
- (iii) Electrophilic addition reaction where attack is done by H^+ (Electrophile)

Question 18

- a)
- (i) Since the monomer is unsaturated will undergo addition polymerisation and the repeating unit of the resulting polymer will be
- $$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C} - \text{C}- \\ | \quad | \\ \text{H} \quad \text{CN} \end{array}$$
- (ii) Addition polymerisation

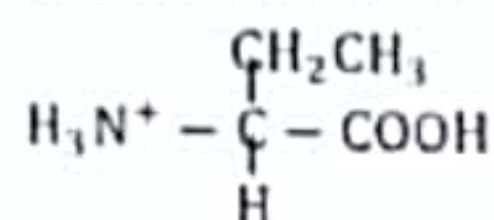
- b) The prefix di in dipeptide indicates that the given compound is dimer ('Polymerisation' with only two monomers) and the linkage is $-\text{CO} - \text{NH} -$ indicating that the compound is diamide (note; peptide is the alternative name for amide)
- Hence the structure of amino acid is obtained by breaking the $\text{CO} - \text{NH}$ link by adding element (which was originally removed from the monomers of amino acids) of water that is OH group on CO and H on NH to give



Hence

- i) Name of the amino acid is 2-aminobutanoic acid

- ii) Structure of amino acid species in the acidic solution



c)

- (i) Molecular formula of the given repeating unit is $C_6H_8O_4$
 - From which ratio of number of C, H, O, is 6:8:4 respectively which give 3:4:2 after simplification by dividing with smallest number in each.

Hence the empirical formula of the repeating unit is $C_3H_4O_2$.

Alternatively;

The molecular formula of the repeating unit is $\text{C}_6\text{H}_8\text{O}_2 = (\text{C}_6\text{H}_4\text{O}_2)_2 = 2 \times (\text{C}_3\text{H}_4\text{O}_2)$

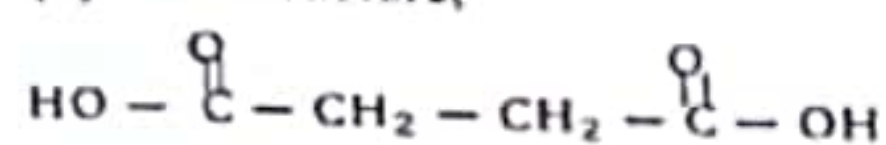
But molecular formula = $n \times$ Empirical formula

That is $C_6H_8O_4 = 2 \times (C_2H_4O_2)$

Where $n = 2$

Hence empirical formula of the repeating unit is $C_3H_4O_2$

- (ii) **Structure:**



Name: Butane - 1,4 - diolc acid (or succinic acid)

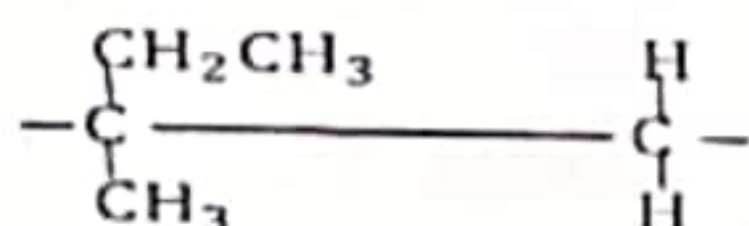
- (iii) Can be hydrolysed.

Question19

a)

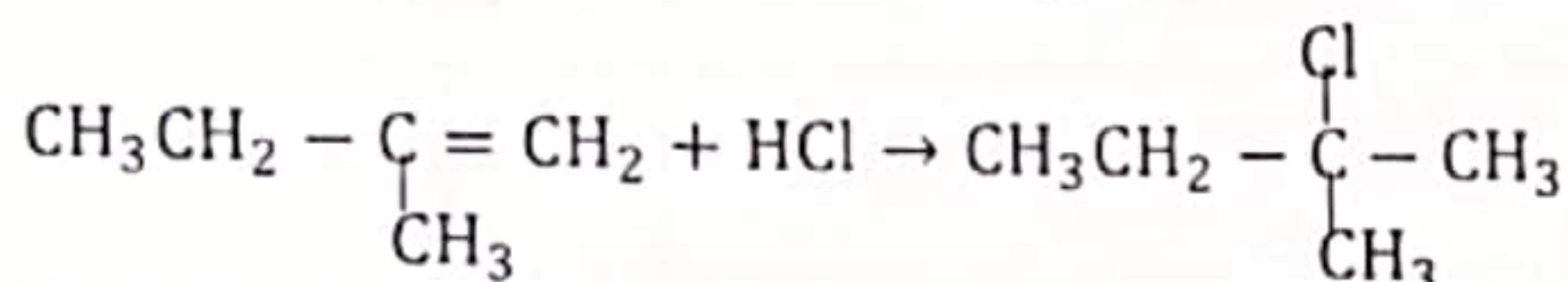
- (i) 2-methylbut-1-ene

(ii)



Type of polymerisation: addition polymerisation

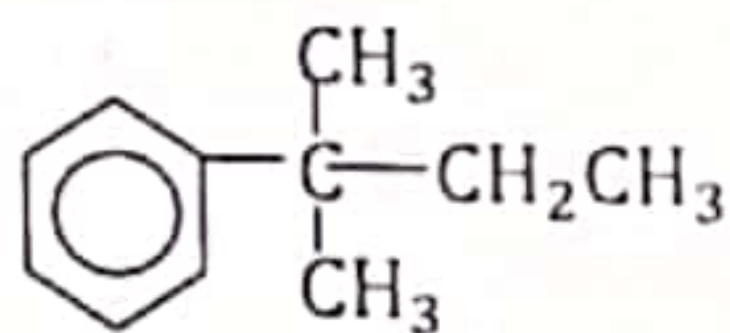
- (iii) With HCl, 2-methylbut-1-ene undergo Markownikoff's addition according to the following



2 - methylbut - 1 - ene

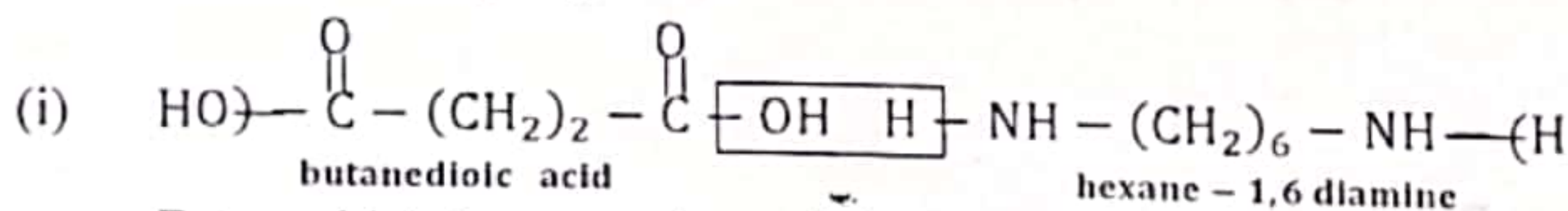
2 - chloro - 2 - methylbutane

Then under presence of AlCl_3 (Lewis acid catalyst) the produced haloalkane will react with benzene in substitution reaction to give the following major product.

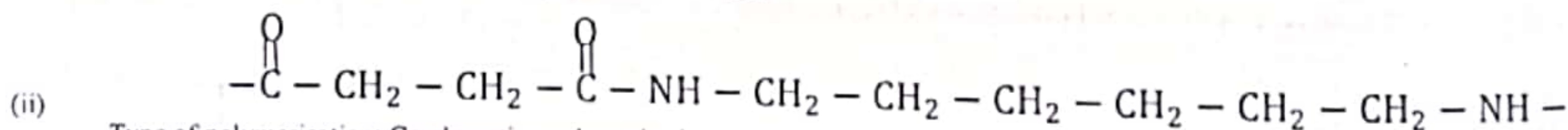


- (iv) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$

b)



From which the repeating unit becomes

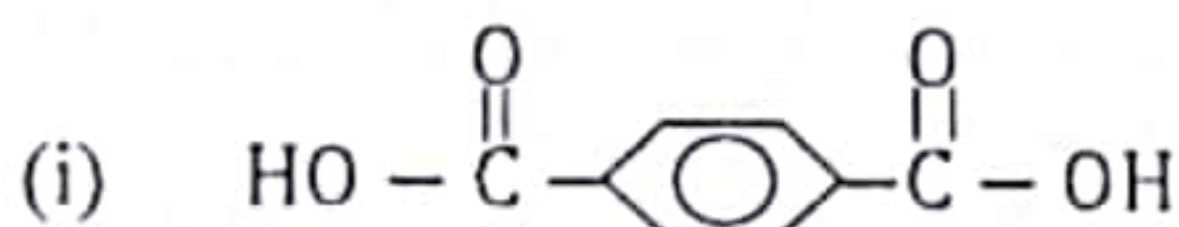


Type of polymerisation; Condensation polymerisation.

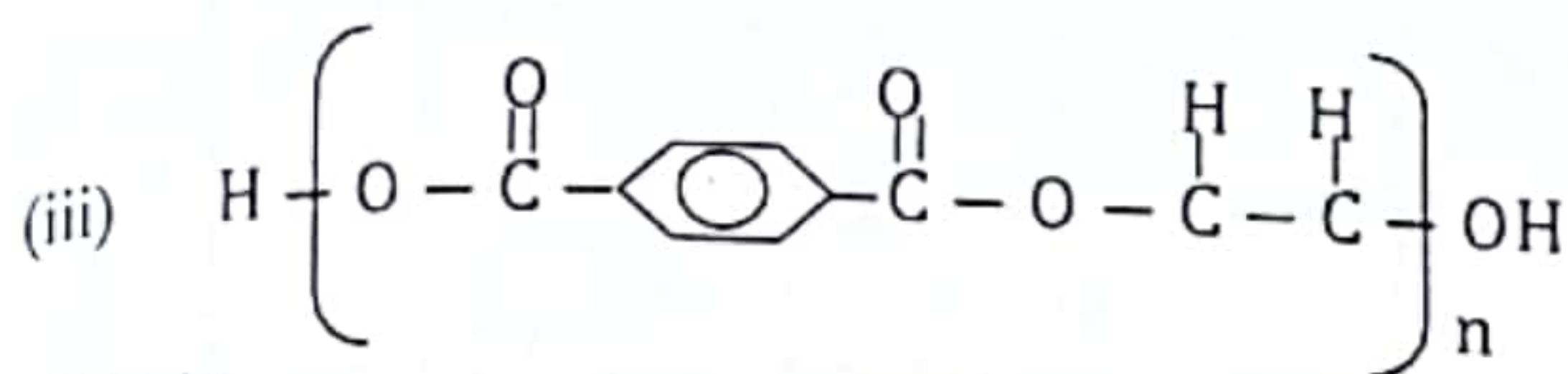
The linkage is -CO-NH- and hence the type of linkage is amide (or peptide).

Question 20

a)



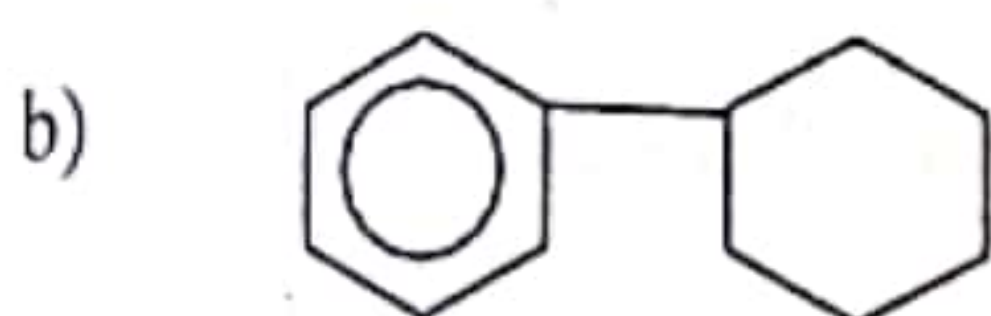
- $$(ii) \quad \begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{HO} - \text{C} - \text{C} - \text{OH} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$



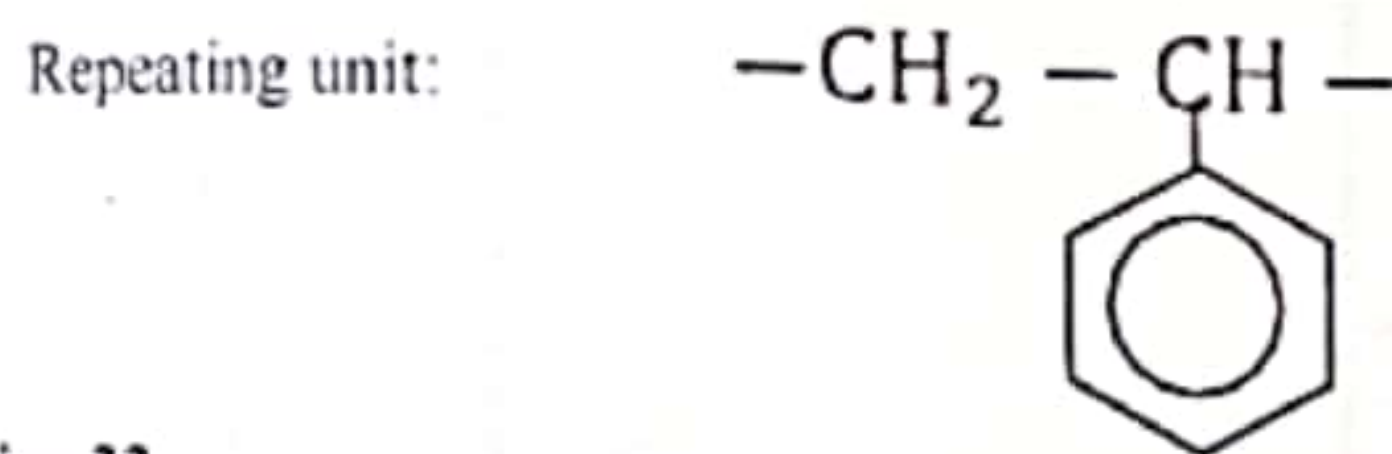
- b) Polyester
- Addition polymer is formed by addition reaction where unsaturated monomer combines to give one product (polymer) only.
 - Small molecules (apart from the polymer) are eliminated in the formation of condensation polymer through condensation reaction.
- c) Polyethene (or polypropene or polystyrene or any other example)

Question 21

- a)
- (i) First substance : HCl (or HBr)
Second substance: AlCl₃ (or AlBr₃ or FeCl₃ or FeBr₃)
- (ii) CH₂ = CH₂ + HCl → CH₃ - CH₂Cl (i)
- (iii) CH₃ - CH₂Cl + AlCl₃ → CH₃ - CH₂⁺ + [AlCl₄]⁻ (ii)
- And the overall reaction equation become (by taking (i) + (ii))
- $$CH_2 = CH_2 + HCl + AlCl_3 \rightarrow CH_3CH_2^+ + [AlCl_4]^-$$
- electrophile



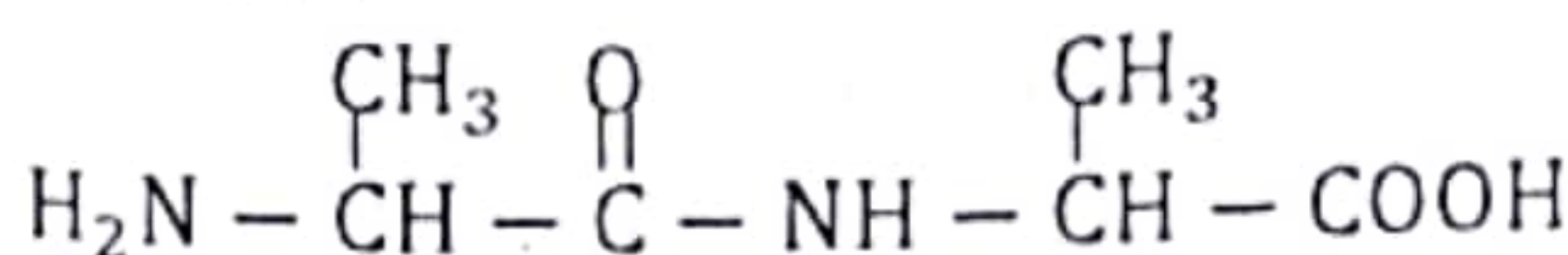
- c) Type of polymerisation: Addition polymerisation



Question 22

- a)
- (i) Hexane - 1,6, - diamine
- (ii) $\text{O}=\text{C} - (\text{CH}_2)_4 - \text{C}=\text{O} - \text{NH} - (\text{CH}_2)_6 - \text{NH} -$
- b)
- (i) $\text{H}_2\text{N} - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \text{COOH}$
- (ii) $\text{H}_2\text{N} - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \text{C}(=\text{O}) - \boxed{O - H \quad H} - \text{N} - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \text{COOH}$
- ↓
- $$\text{H}_2\text{N} - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \text{C}(=\text{O}) - \text{NH} - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \text{COOH}$$

Hence the correct structure is



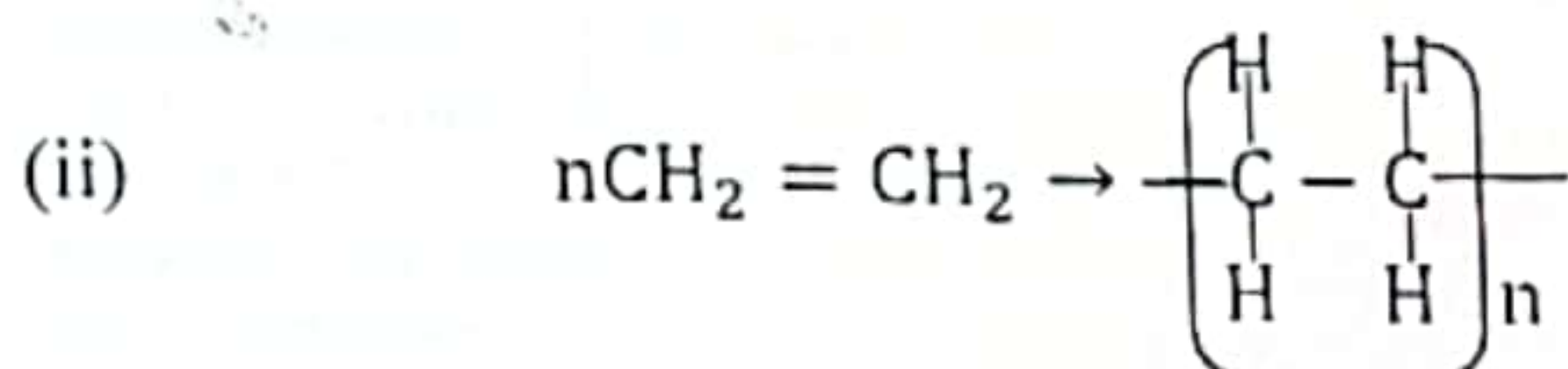
- c)
- (i) Quaternary ammonium bromide salt
- (ii) Reagent: CH₃Br (bromomethane)
Condition: CH₃Br must be in excess
- (iii) Nucleophilic substitution reaction

Question 23

- a) $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl} + \text{KOH}(\text{Conc.}) \xrightarrow[90^\circ\text{C}]{\text{C}_2\text{H}_5\text{OH}} \begin{array}{c} \text{H} \quad \text{Cl} \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} + \text{KCl} + \text{H}_2\text{O}$
- b) Ester
- c)
- $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$
 - High electron density of the double bond repels the incoming nucleophile

Question 24

- a)
- Refer to the text



- b) 1,2-dibromoethane
- c) Type of the reaction Electrophilic addition reaction
Equation: $\text{CH}_2 = \text{CH}_2 + \text{Br}_2 \rightarrow \text{Br}-\text{CH}_2-\text{CH}_2-\text{Br}$
- d)

Elements	C	H	O
Mass of each in 100g of compound	38.71g	9.68g	9.68g
$n = m/M_r$	$\frac{38.71}{12} = 3.2258$	$\frac{9.68}{1} = 9.68$	$\frac{51.61}{16} = 3.2256$
Divide by the smallest	$\frac{3.2258}{3.2256} \text{ mol}$	$\frac{9.68}{3.2256} \text{ mol}$	$\frac{3.2256}{3.2256} \text{ mol}$
Simplest ratio	1	3	1

Hence empirical formula of the compound is CH_3O

Let, molecule formula be $(\text{CH}_3\text{O})_n = \text{C}_n\text{H}_{3n}\text{O}_n$

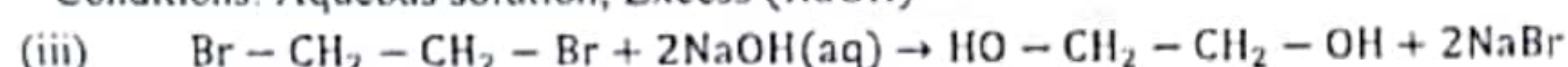
Then the $12n + 3n + 16n = M_r = 62$

$$31n = 62 \text{ or } n = 2$$

Hence molecule formula of D is $\text{C}_2\text{H}_6\text{O}_2$

(ii) Reagent: NaOH

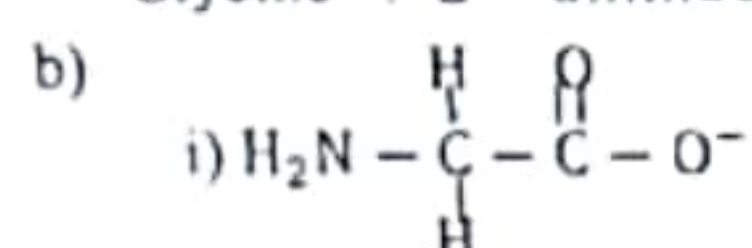
Conditions: Aqueous solution, Excess (NaOH)



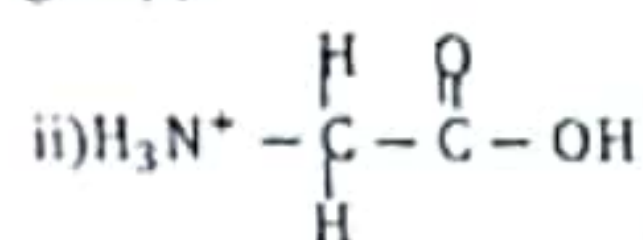
Question 25

a) Alanine : 2-aminopropanoic acid

Glycine : 2-aminoethanoic acid

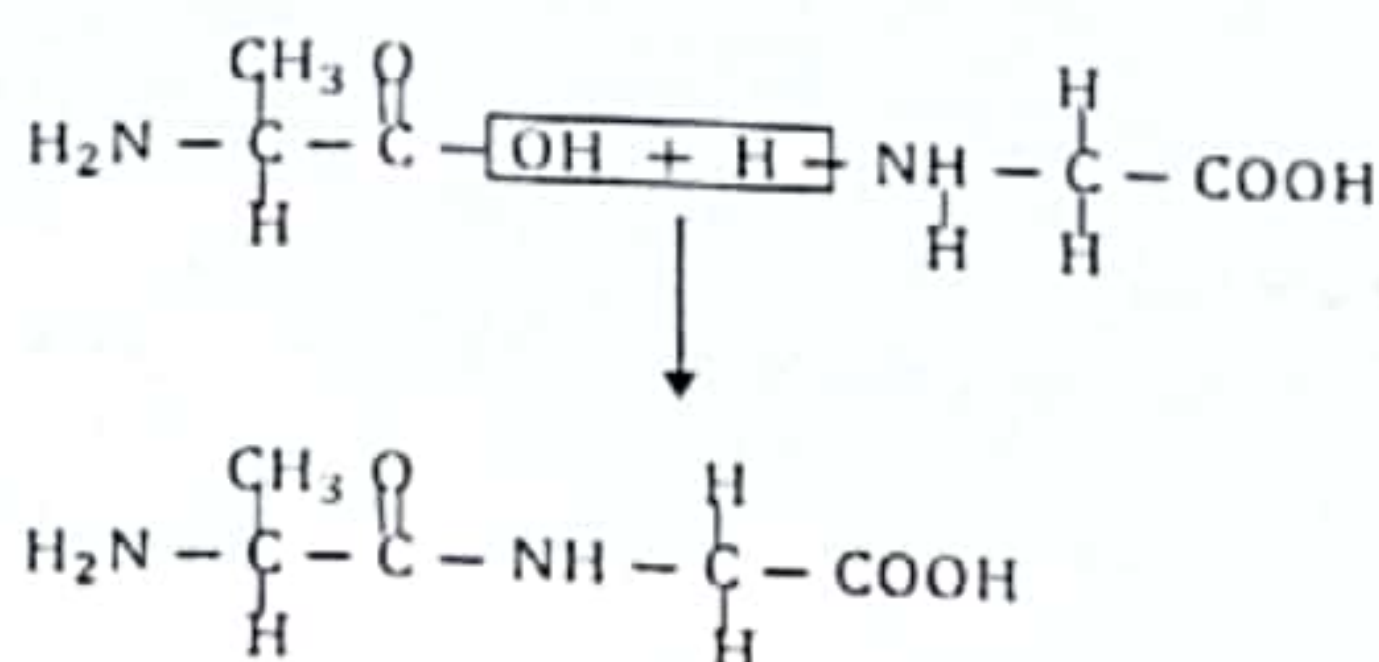


(Note: At pH 14, the solution is alkaline and therefore the glycine will act as an acid by donating hydrogen proton through the carboxylic group).

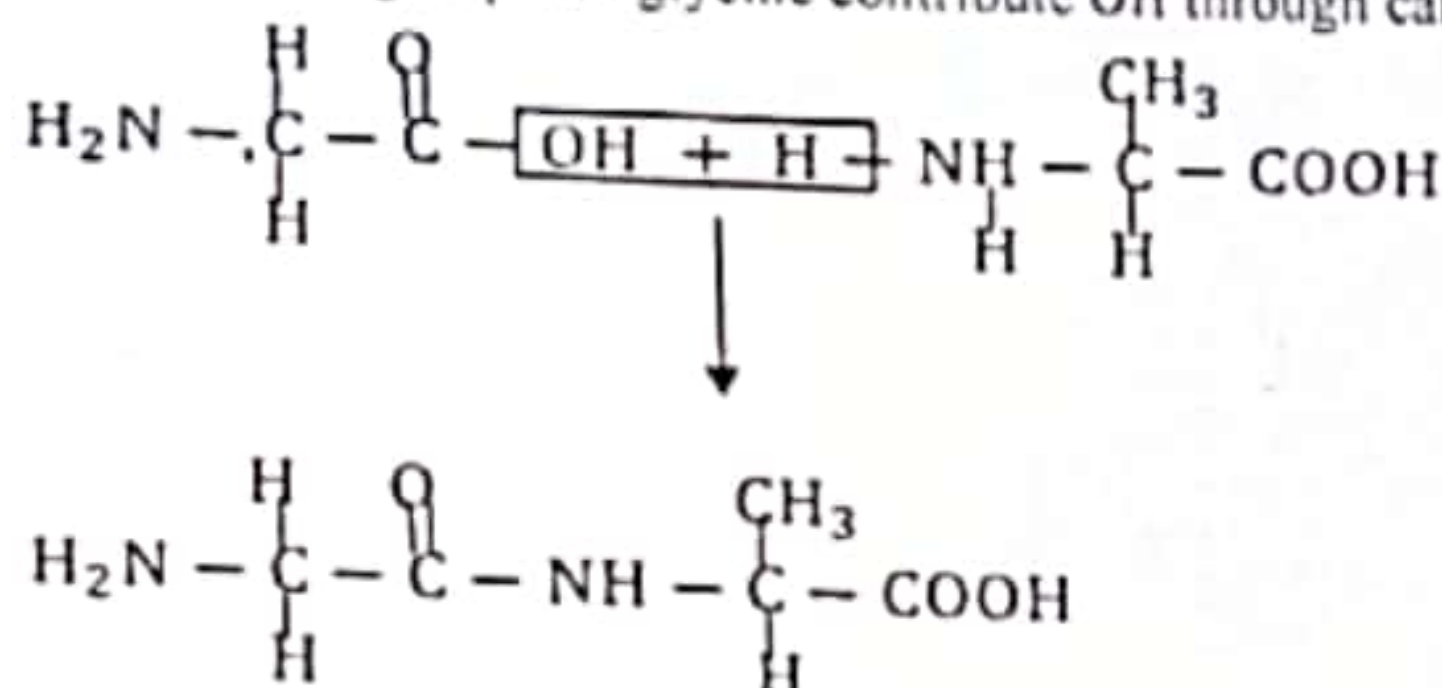


(At pH 2, the solution is acidic and therefore will act as a base by an amino group accepting hydrogen proton)

c) First peptide: If alanine contribute OH through carboxylic group and glycine contribute H through amino group to eliminate H_2O

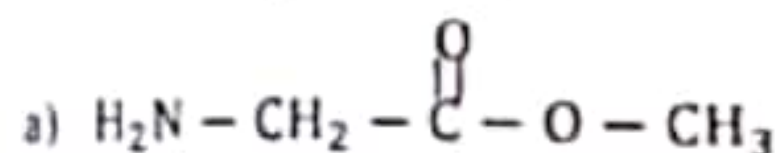


Second peptide: If alanine contribute H through amino group and glycine contribute OH through carboxylic group to eliminate H_2O



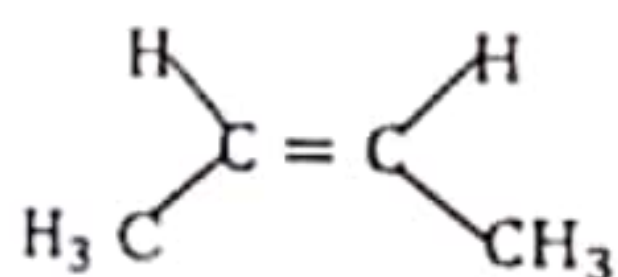
Hence the two peptides

- $\text{H}_2\text{N}-\underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{CH}_2-\text{COOH}$ and
- $\text{H}_2\text{N}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}}-\text{COOH}$



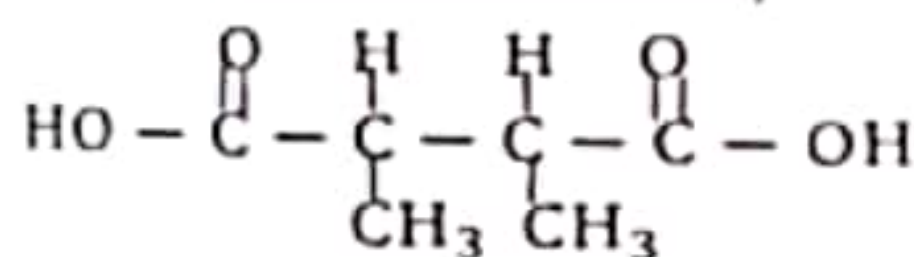
Question 26

a) Monomer



Type of polymerisation: Addition polymerisation

b) For first monomer: Structure is;

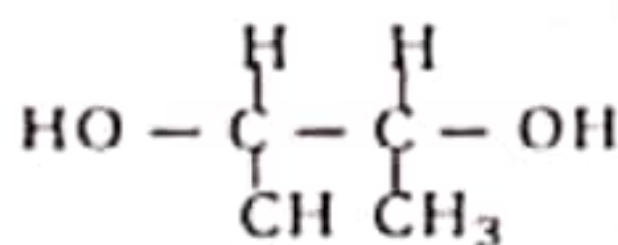


(You may replace OH with Cl and it become diacyl chloride)

Its name is 2,3 - dimethylbutane - 1,4 - dioic acid

For second monomer:

Structure is



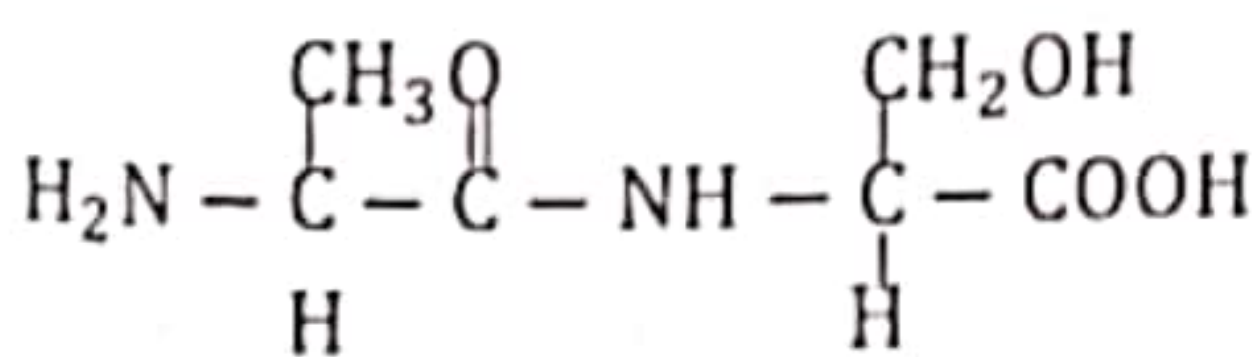
(The same as writing $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$)

Its name is butane - 1,2 - diol

Type of polymerisation: Condensation polymerisation

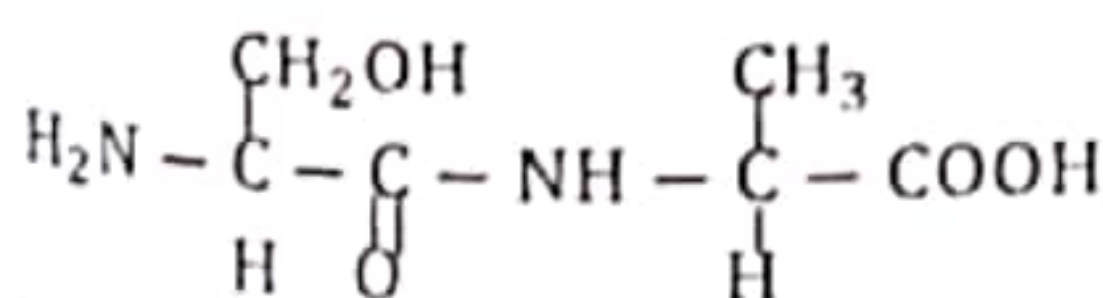
iii) NaOH

b) First structure is:



(This is formed when structure 1 loses OH of COOH)

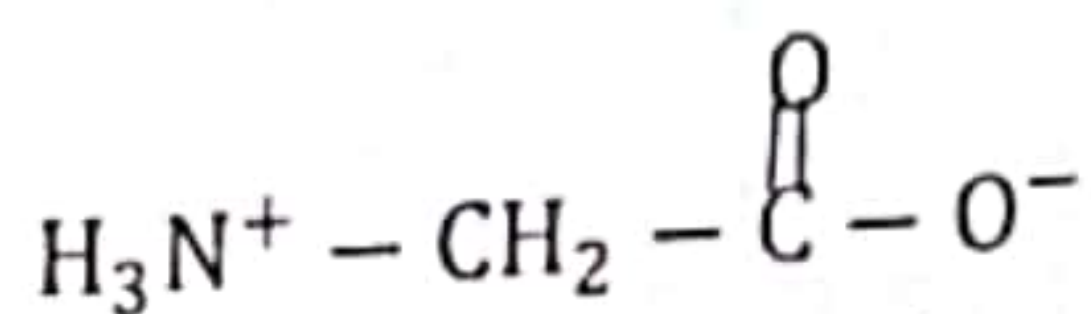
Second structure is:



(This is formed when structure 2 loses OH of COOH)

Question 27

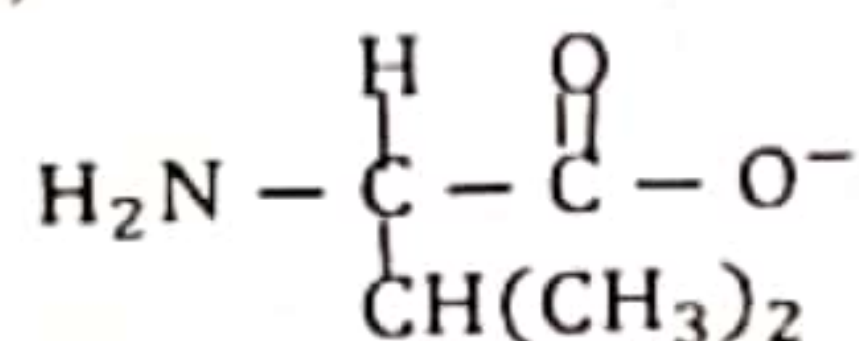
- a) Types of the polymer; Polyamide
Type of polymerisation: Condensation
- b) 'Solid' suggests that there is very strong inter molecular forces of attraction in aminoethanoic acid which is ionic bond (electrostatic force of attraction between cations and anions)
- This is due to the fact, amino group is strong basic enough to accept hydrogen proton from carboxylic group resulting to the following specie:



- c) Ionic bonding in aminoethanoic acid is stronger intermolecular forces of attraction than hydrogen bonding in hydroxyethanoic acid.

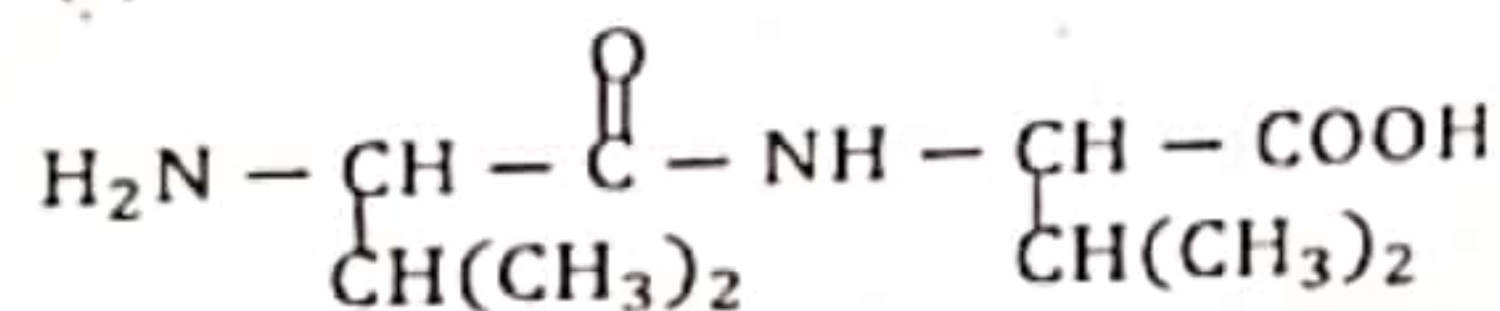
Question 28

(i)



(At pH 12 the solution is basic and the amino acid donate H^+ through carboxylic group)

(ii)

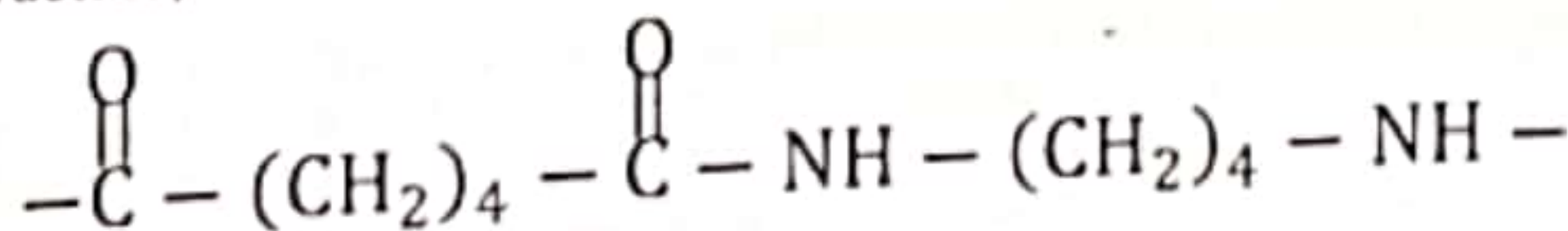


- (iii) Intra-hydrogen bonding (or intramolecular hydrogen bonding)

Question 29

- a) Name: butane – 1,4 – diamine
A: $\text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$ (or $\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{Br}$)
B: $\text{N} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{C} \equiv \text{N}$
For steps 1: Cl_2 (or Br_2)
For step 2: KCN
For step 3: LiAlH_4
Type of reaction: Reduction

- b) Structure;

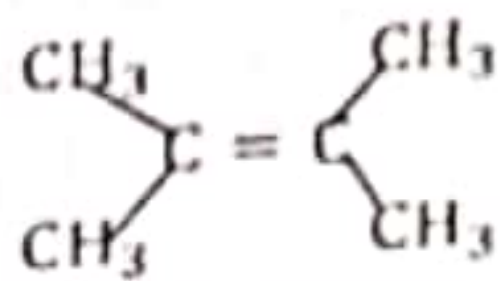


Type of interaction: Hydrogen bonding.

Question 30

a)

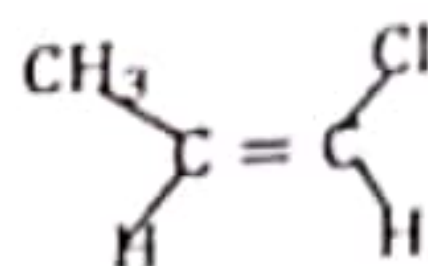
(i)



- (ii) Poly (2,3 – dimethylbut – 2 – ene)

b)

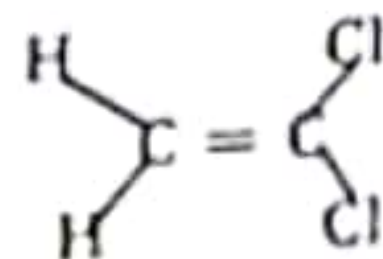
(i)



- (ii) Poly(1-chloropropene)

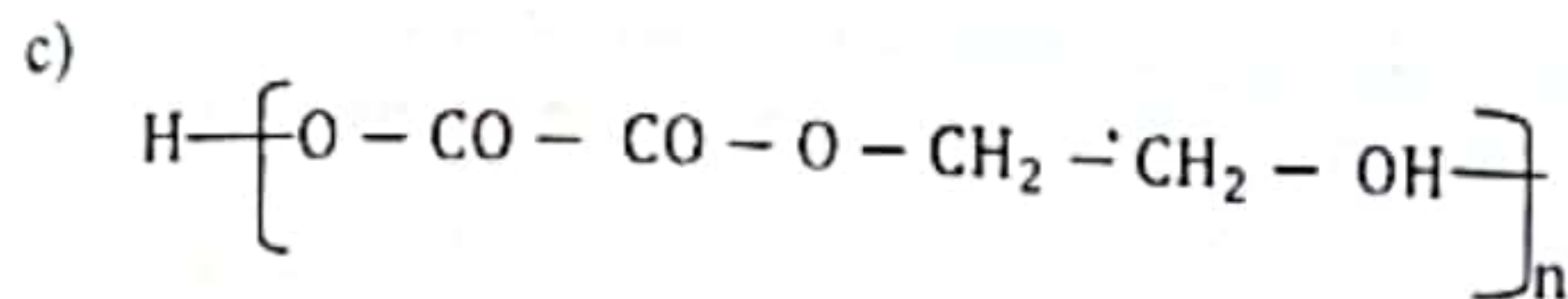
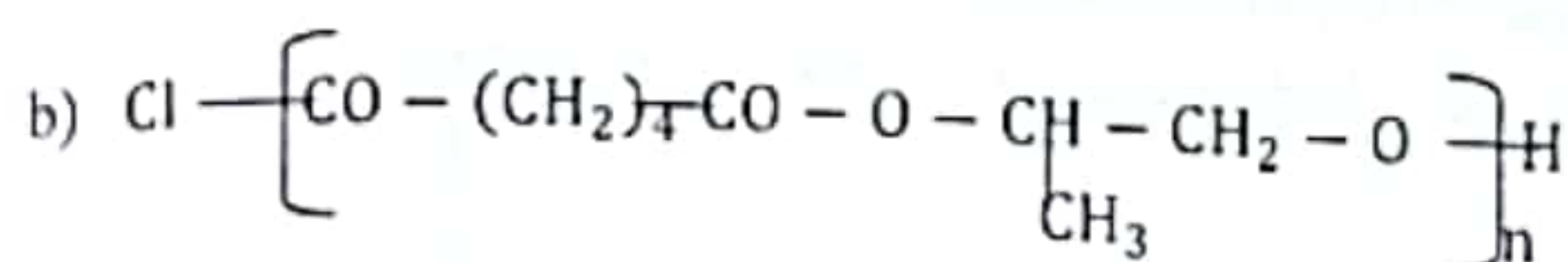
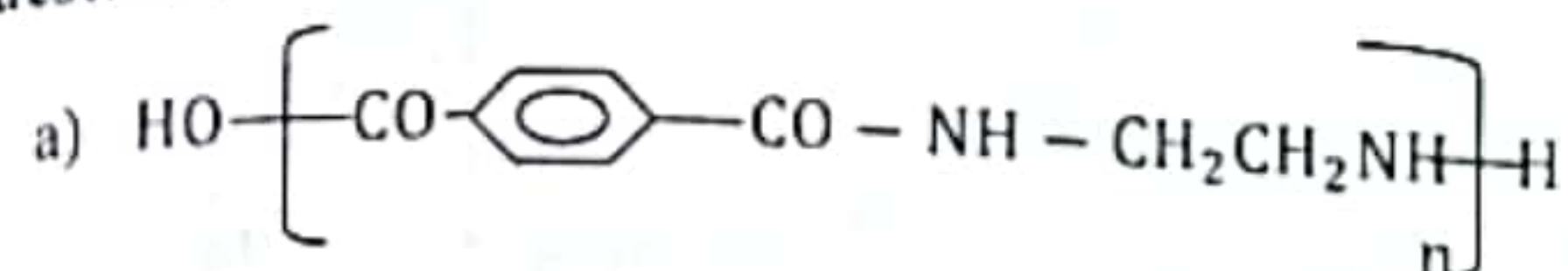
c)

(i)



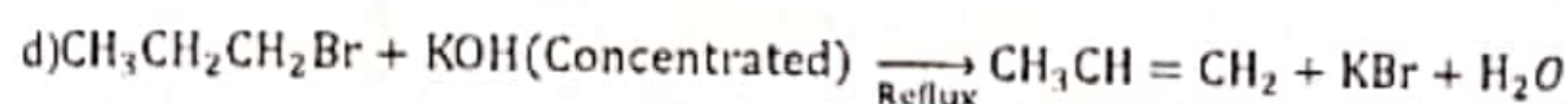
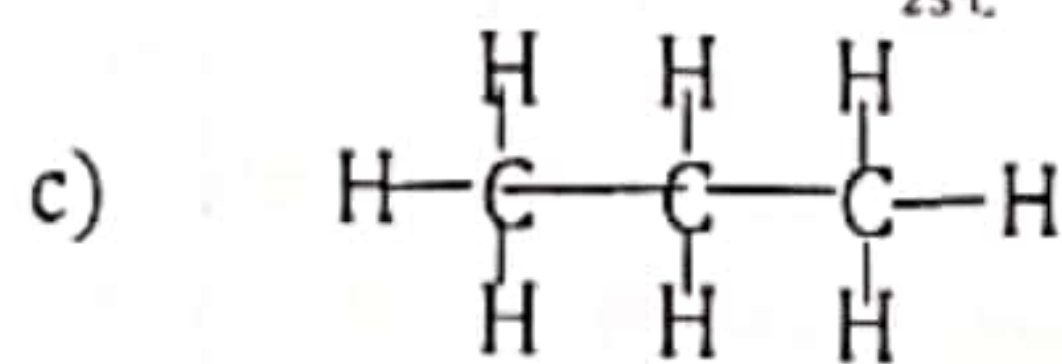
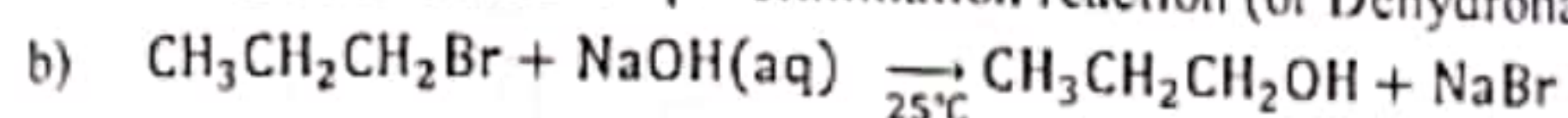
- (ii) Poly(1,1-dichloroethene)

Question 31



Question 32

- a) A: Free radical substitution reaction
 B: Nucleophilic substitution reaction
 C: Nucleophilic substitution reaction
 D: Base induced β - elimination reaction (or Dehydrohalogenation)



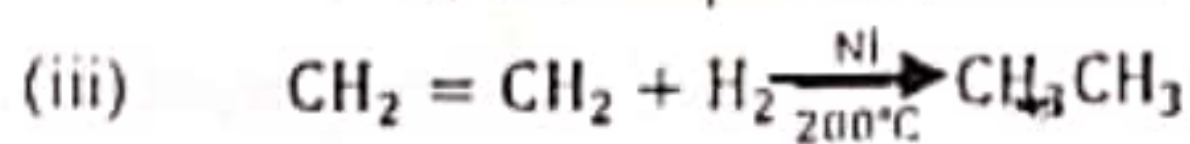
e) Propan - 1 - ol

Question 33

- a) Nucleophilic substitution reaction
 b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Question 34

- a)
 (i) $\text{CH}_2 = \text{CH}_2$
 (ii) The Ethylene liberated by banana ages the cabbage
- b)
 (i) C_nH_{2n}
 (ii) A: Free radical substitution reaction
 B: Electrophilic addition reaction (or hydrogenation)
 C: Acidic Induced β - elimination reaction
 D: Electrophilic addition reaction (or hydration)
 E: Base induced β - elimination reaction
 F: Electrophilic addition reaction
 G: Nucleophilic substitution reaction
 H: Nucleophilic substitution reaction

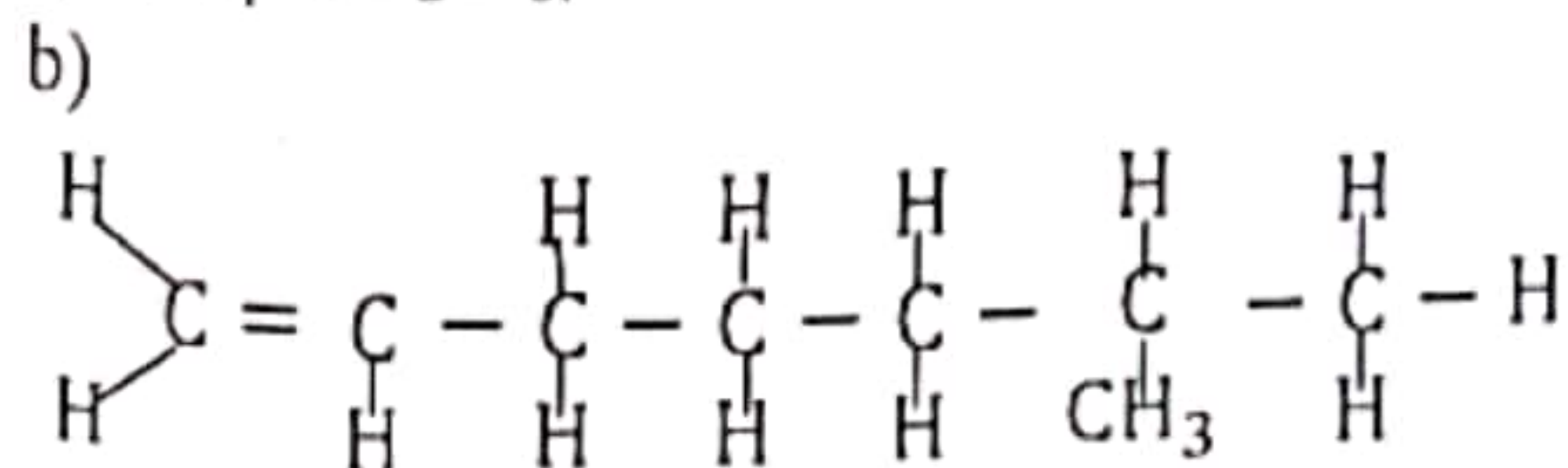


(iv) HBr (Hydrogen bromide)

- c)
 (i) In E the base is **concentrated** while in G it is **dilute**
 (ii) Dehalohydrogenation (or dehydrohalogenation)

Question 35

a) Propan - 2 - ol



- c) Amide
- d) Function isomer of A is $\text{CH}_3\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_3$
Hence the name of the isomer is methyl propanoate
- c) Amines are base while lemon juice is an acid. Therefore neutralisation reaction takes place to eliminate the smell.

Question 36

a) Refer to the text

b) First isomer : $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{OH}$
Name: Ethanoic acid

Second isomer: $\text{H} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{OCH}_3$
Name: methyl methanoate

- c)
- (i) Ethanoic has higher boiling point
Reason:
Hydrogen bonds between ethanoic acid molecules are stronger intermolecular force of attraction than Van-der Waals force between ester molecules
- (ii) Methyl methanoate has higher vapours pressure
Reason:
The Van-der Waals forces between the ester molecules are weaker than the hydrogen bonds between ethanoic acid molecules

Question 37

a)

- (i) Unsaturated
It contains $\text{C} = \text{C}$
- (ii) $\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH} = \text{CH}_2$

b) Addition polymerisation

c)

- Destruction of forests (leading to global warming)
- Rubber is not biodegradable
- Burning rubber release toxic gases

d)

- Making of tyres for cars
- Making of gloves and other important tools in medical industry
- Making of raincoats

Question 38

- a) Elimination reaction
- b) Alkene
- c) Electrophilic addition reaction
- d)

- i) Structure of P is $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$
- ii) Structure of Q is $\text{CH}_3\text{CH} = \text{CHCH}_3$

e) Q

Reason:

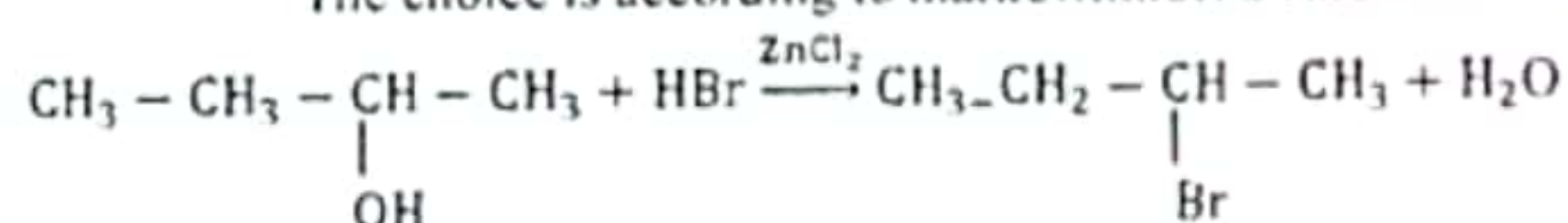
Q contain greater number of alkyl groups at double bond, $\text{C} = \text{C}$ (Q has two alkyl groups while P contain only one alkyl group) and therefore according to Saytzeff's rule, Q is more stable

f)

(i) Structure of X is $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$

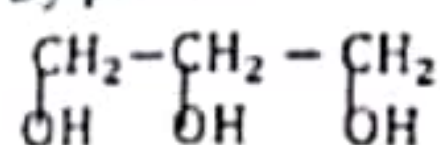
(ii) Structure of Y is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
The major product is X

The choice is according to markownikoff's rule which state that (Refer to the text).



Question 39

- Sodium salt of long chain carboxylic acid
By product



Question 40

- (i) Q
Reason:
In P, Cl is directly bonded to benzene during and therefore there is formation of $-\text{C}=\text{Cl}$ due to mesomerism making the Cl poor leaving group unlike in Q
- (ii) A
Reason:
I in A is better leaving group due to its larger size than Cl in B
- (iii) Y
Reason:
Y being primary haloalkane, its carbon with experience weaker steric hindrance than X which is secondary
- (iv) S
Reason:
In R, the carbon with Cl has high electron density in $\text{C}=\text{C}$ thus exerting large repulsion to incoming nucleophile unlike in S where C with Cl has no $\text{C}=\text{C}$.

Question 41

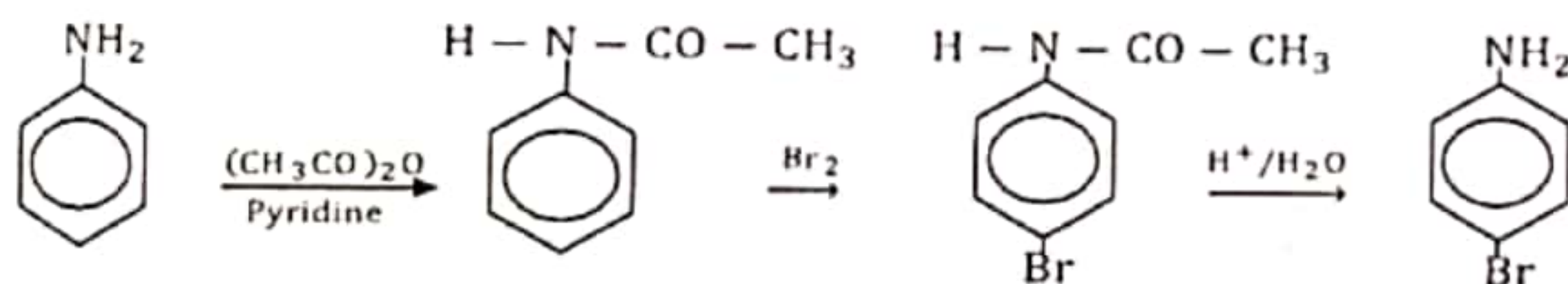
KCN is ionic provide cyanide ions $\text{N} \equiv \text{C}^-$ in solution. Although both carbon and nitrogen are in a position to donate lone pairs, the attack takes place mainly through carbon atom because lone pair in negatively charged atom (carbon atom) are more reactive than lone pair in the neutral atom (Nitrogen atom) and $\text{C}-\text{C}$ is more stable than $\text{C}-\text{N}$. However, AgCN is mainly covalent and therefore only nitrogen atom is free to donate its lone pair forming isocyanides as the chief product.

Question 42

Propan-1-ol > 4-methylphenol > phenol > 3-nitrophenol > 3,5-dinitrophenol > 2,4,6-trinitrophenol

Question 43

This can be done by protecting the amino ($-\text{NH}_2$) group by acylation with acetic anhydride (or ethanoyl chloride), then carry out the required substitution followed by hydrolysis of the substituted amide to the substituted amine as shown below



Question 44

$\text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}$

Hint: consider positive inductive effect and steric effect

Question 45

In both cases, due to polar $\text{O}-\text{H}$ bond alcohol and water behave as acids but in alcohols due to presence of alkyl groups which exerts positive inductive effect, the $\text{O}-\text{H}$ bond become less polarised and the alkoxide ion become more unstable than hydroxide ion.

Question 46

The commercial ethanol is mixed with CuSO_4 and pyridine to make it unfit for drinking (the process is known as denaturation of alcohol).

Question 47

Alcohol better Bronsted bases (electron acceptor) as it has localized lone pairs while lone pairs phenol has been delocalized in mesomerism.

Question 48

CS_2 (Carbon disulphide) is non polar solvent whereas water is polar solvent. In the presence of polar solvent phenol polarizes and give more electrophilic substitution reaction

Question 49

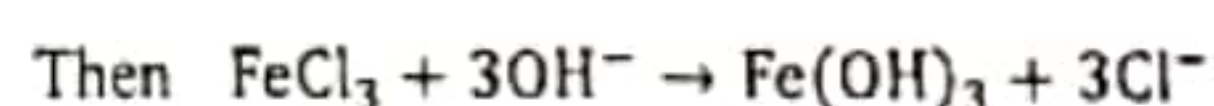
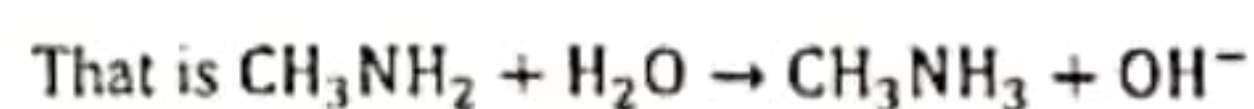
O-Nitrophenol is steam volatile because it possess intra-hydrogen bonding while p-nitrophenol has inter-hydrogen bonding

Question 50

Carbonyl group in carboxylic acid is resonance stabilised as carboxylate ion (there is mesomerism in carboxylic group) and therefore it cannot give nucleophilic addition reaction (characteristic chemical reaction of carbonyl compounds) given by aldehydes and ketones.

Question 51

Methylamine being basic in nature, accept protons from water and in the process, hydroxide ions are formed which reacts with ferric chloride to form insoluble ferric hydroxide.

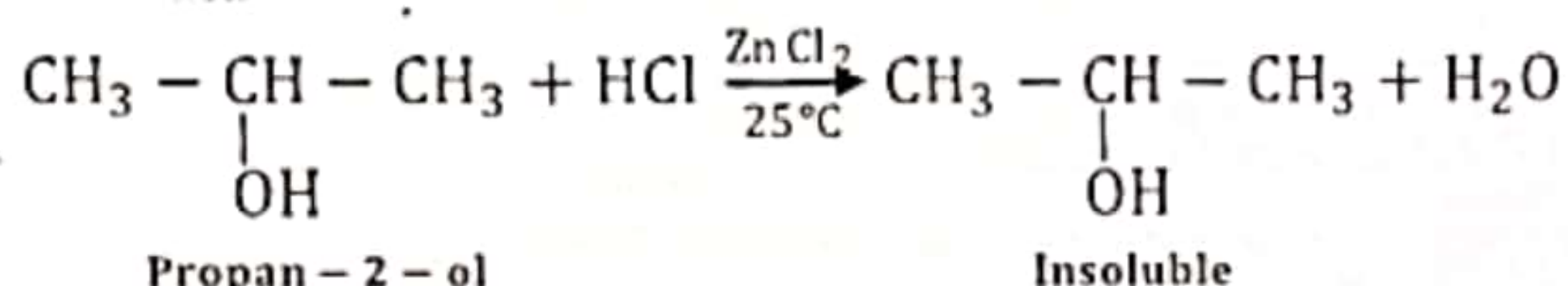


Question 52

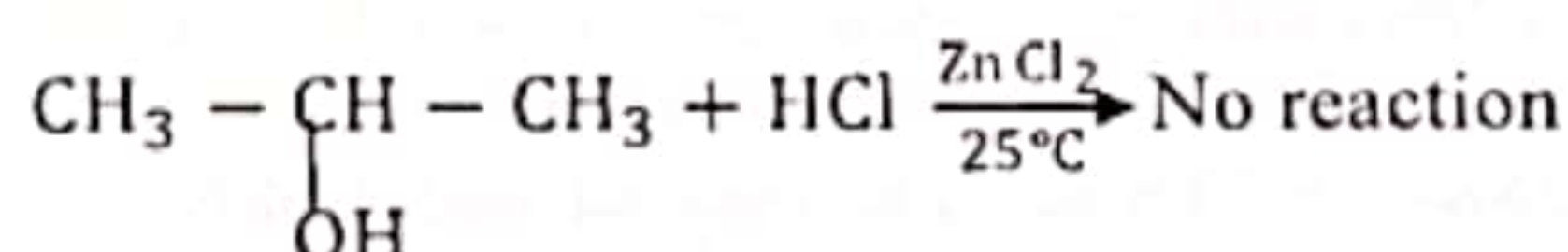
The formation of ester by the given method is reversible reaction to prevent backward reaction, it is distilled out immediately.

Question 53

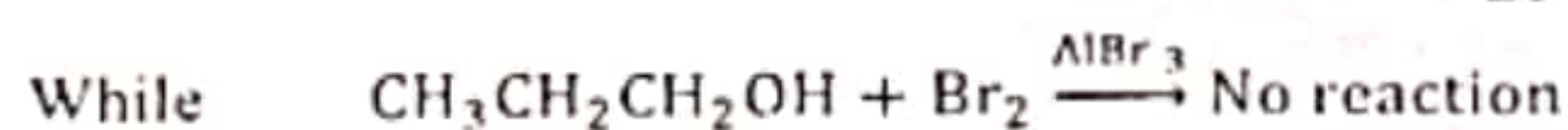
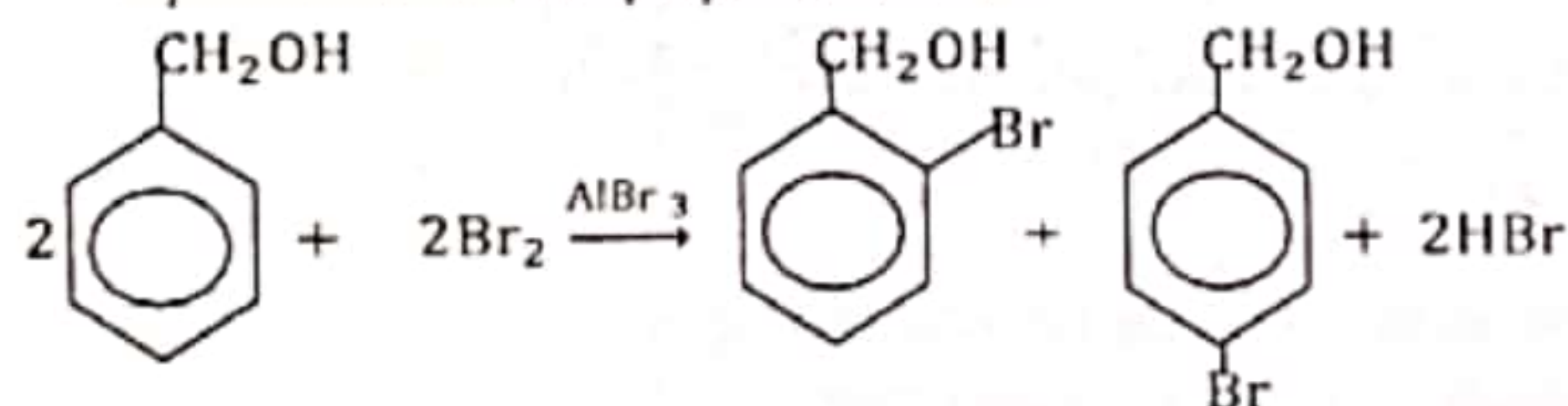
- i) **Lucas test:** with Lucas reagent, propan-2-ol give turbidity (insoluble – cloudiness) within 5 minutes while ethanol does not.



While

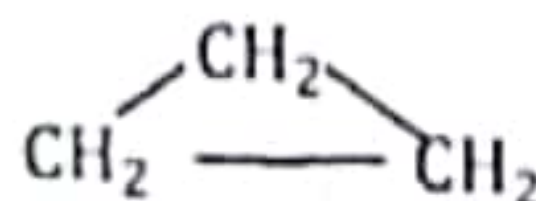
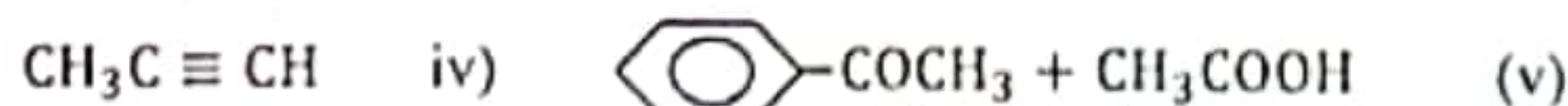
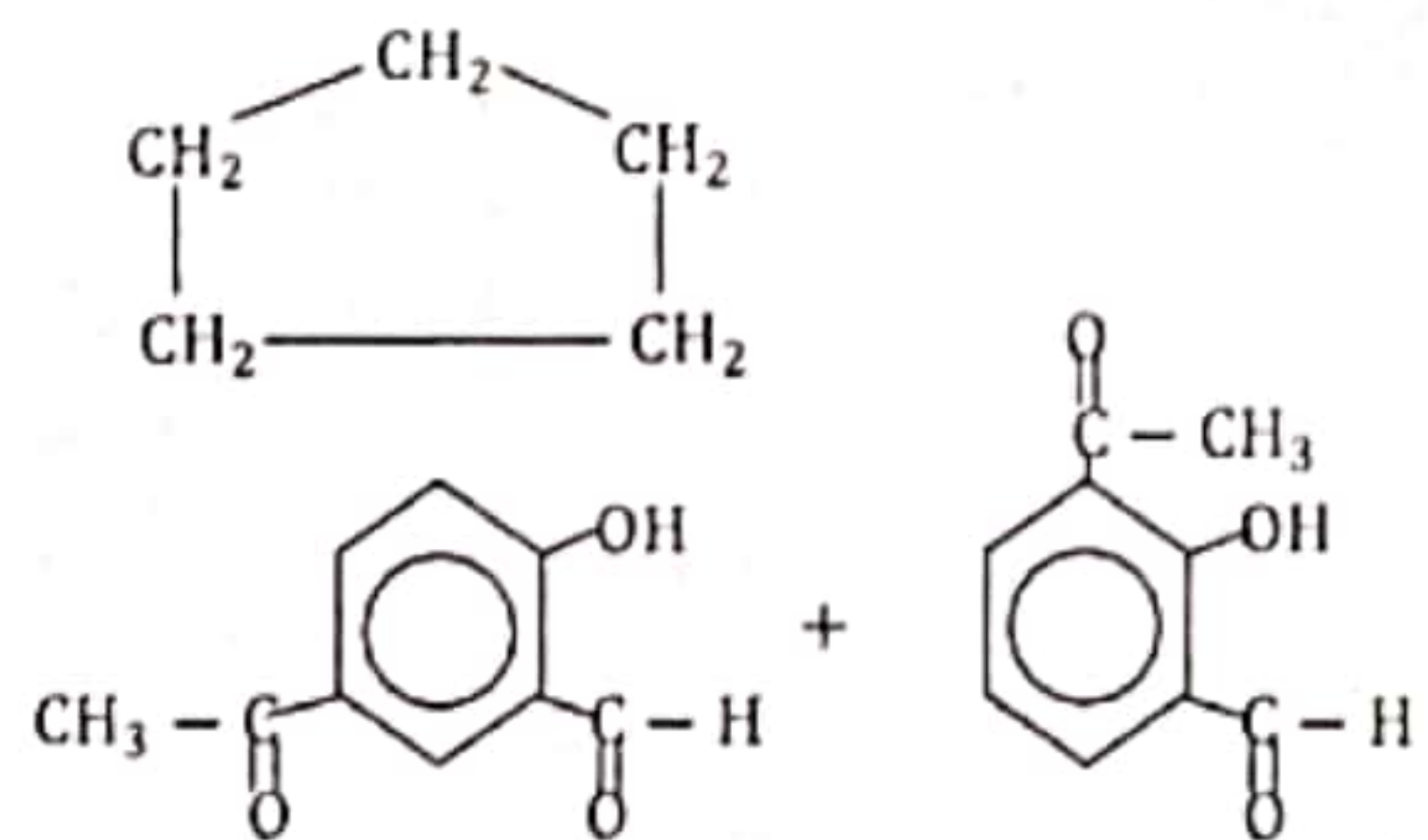


- ii) **Liquid bromine test:** In presence of AlBr_3 (Lewis acid catalyst) benzyl alcohol decolourizes reddish-brown colouration of liquid bromine while propanol does not.



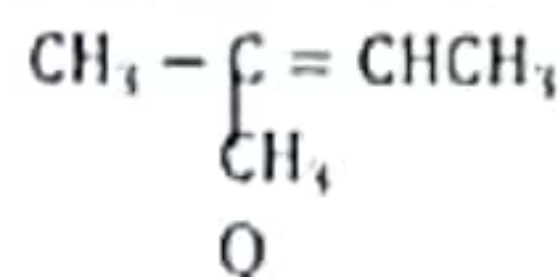
Question 54

a)

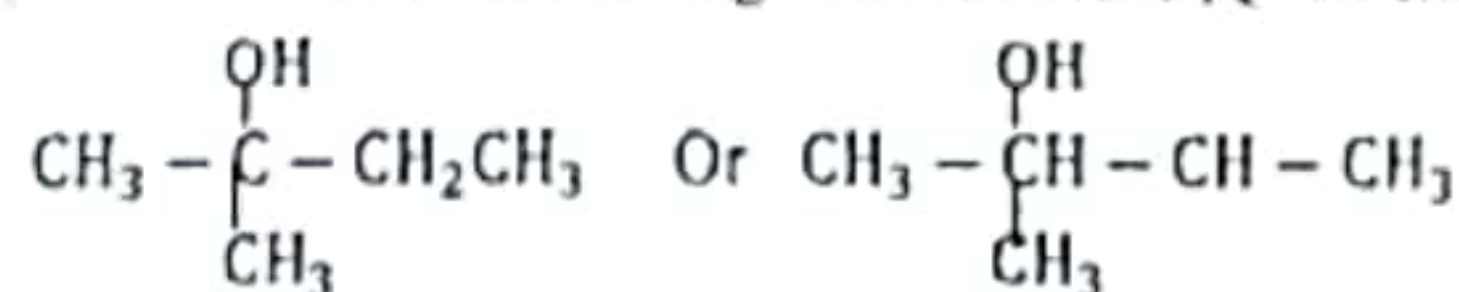


(b)

- Productions obtained on the ozonolysis suggest that structure of alkenes (Q) is

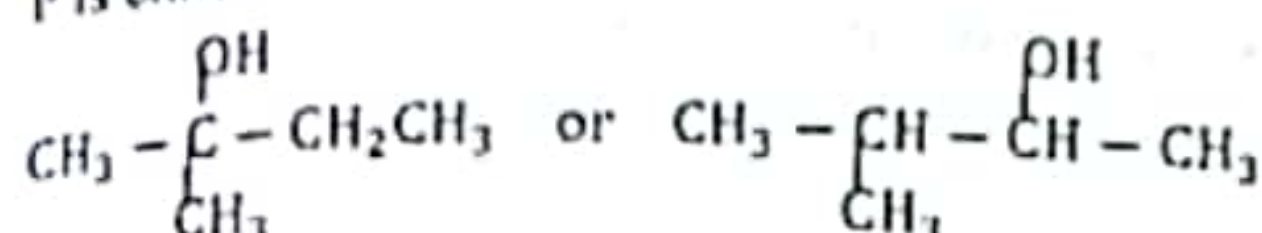


- Alcohol which gives the alkene, Q on elimination reaction is



Hence

P is either



Question 55

- i) A: $\text{CH}_3\text{C} \equiv \text{C} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$
- ii) B: $\text{C}_6\text{H}_5 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$
- iii) C: $\text{C}_6\text{H}_5 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$
- iv) D: $\text{CH}_3\text{CH}_2 - \text{CO} - \text{NH}_2$
- v) E: $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2$
- vi) F: $\text{CH}_3\text{C} \equiv \text{CH}$

Question 57

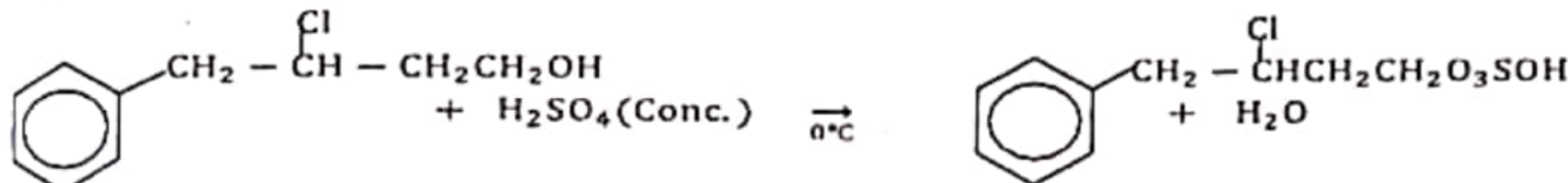
- i) NaOH(aq) followed by addition of $\text{AgNO}_3(\text{aq})$
- ii) NaOH(aq) followed by addition of $\text{AgNO}_3(\text{aq})$

Question 58

a)



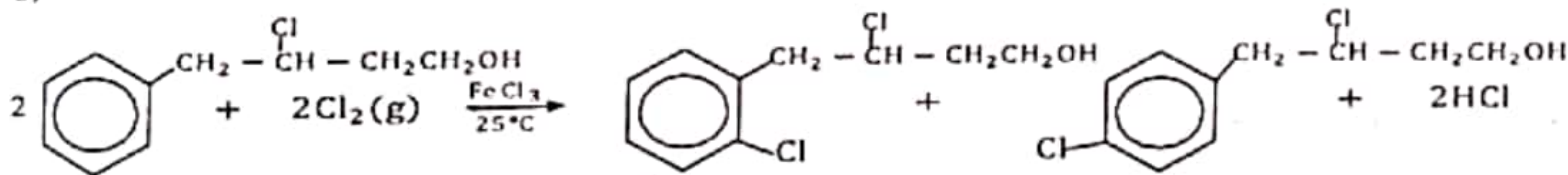
b)



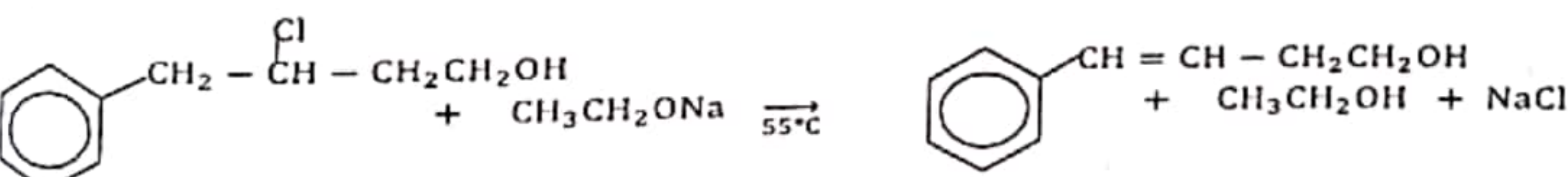
c)



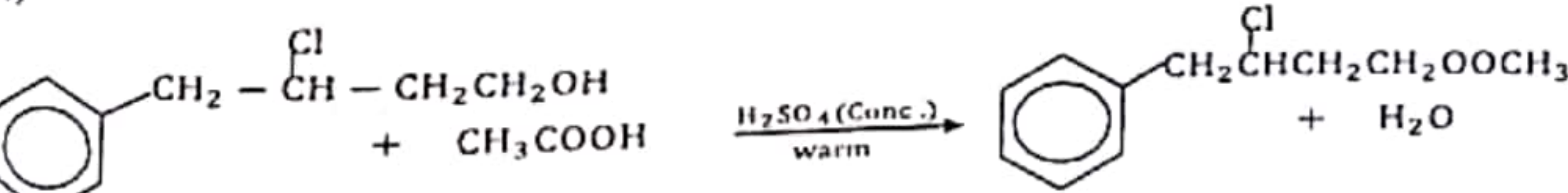
d)



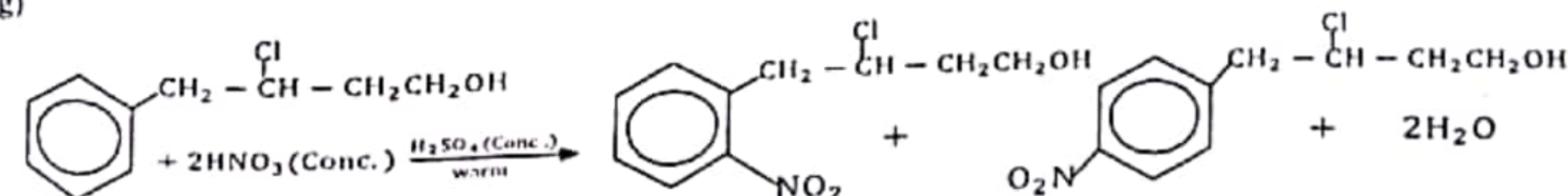
e)



f)

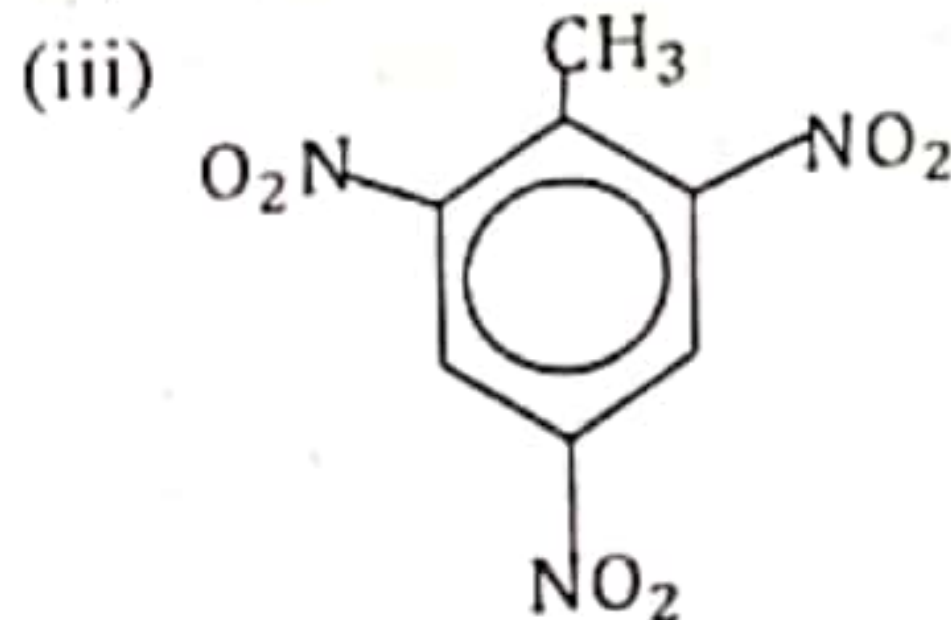
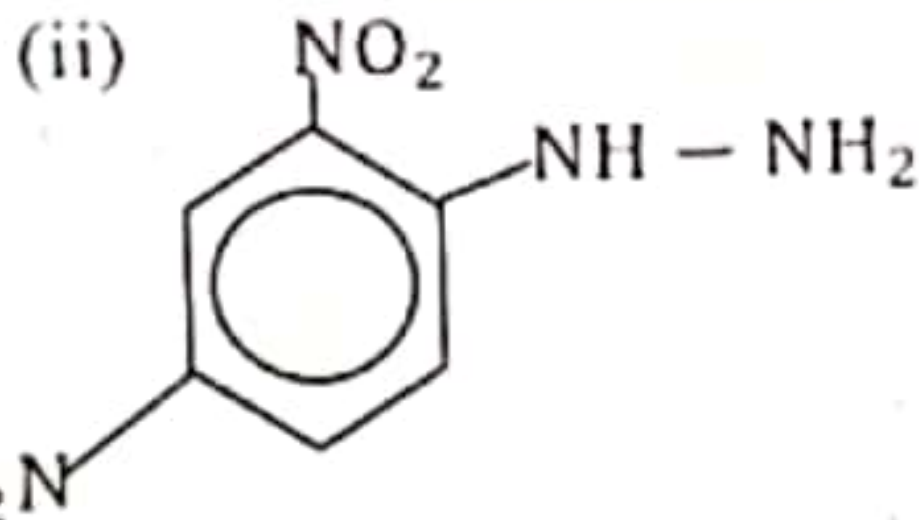
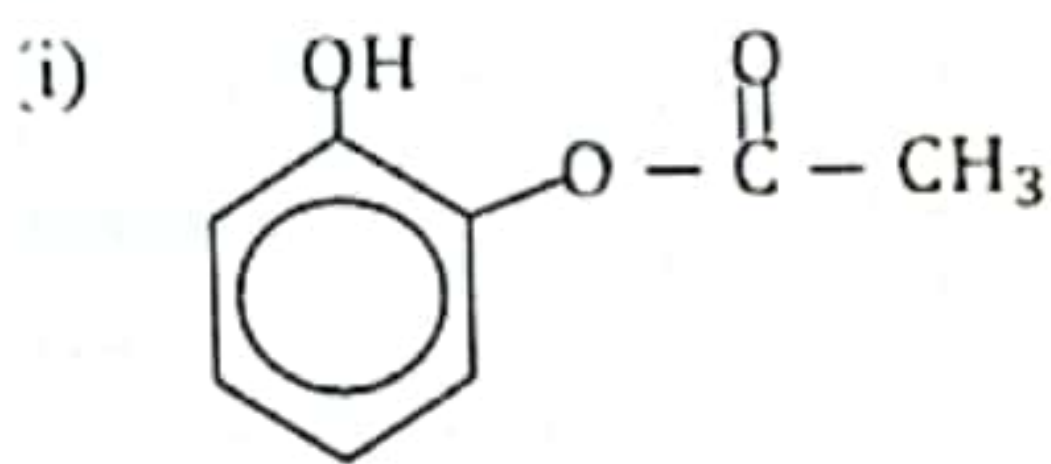


g)

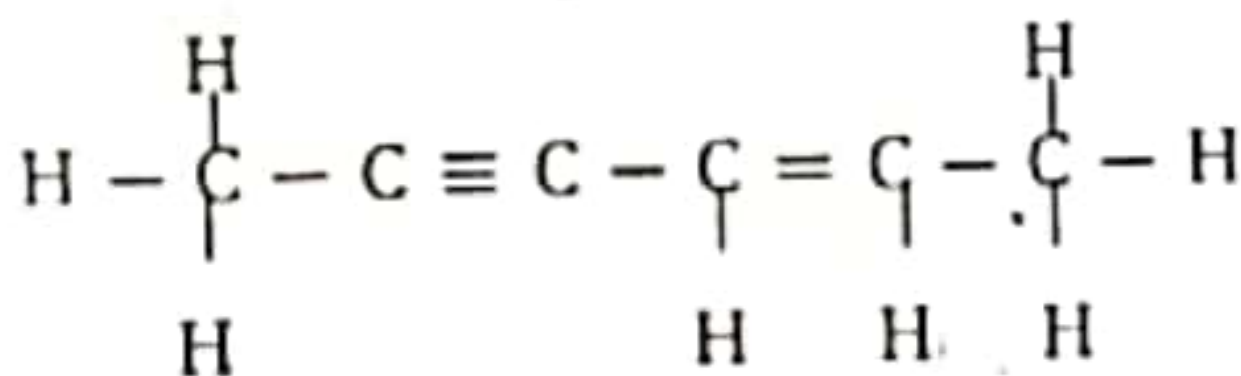


Question 59

a.



ii)



(b) Hints :

- bromine water test (or other suitable test)
- ammonical silver nitrate test (or ammonical copper (I) hydroxide test)
- Fehling's solution test (or any other suitable test)
- Bromine water test (or any other suitable test)

Question 60

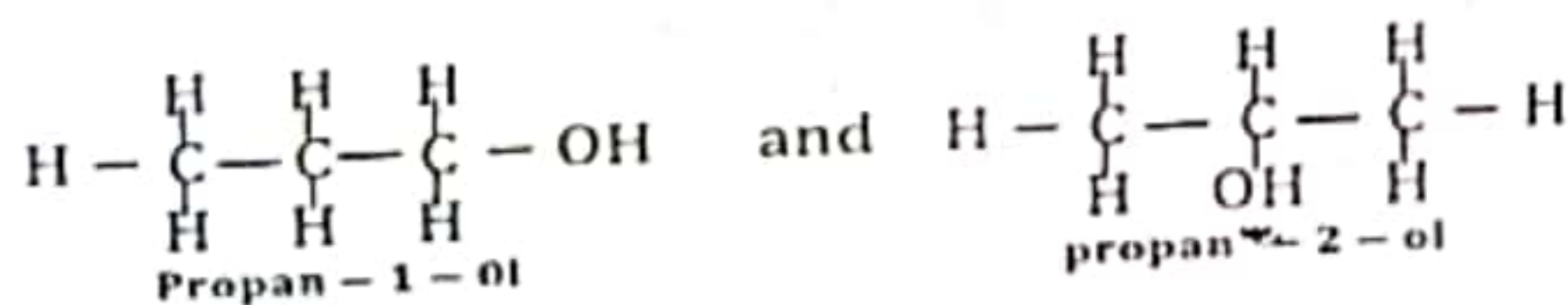
a)

(i)

Elements	C	H	O
Mass of each in 100g of the compound	60g	13.3g	26.7g
Number of mole of each $n = \frac{m}{M_r}$	$\frac{60g}{12g/mol} = 5mol$	$\frac{13.3g}{1g/mol} = 13.3mol$	$\frac{26.7g}{16g/mol} = 1.66875mol$
Divide by smallest to get simple ratio	$\frac{5mol}{1.66875mol} = 3$	$\frac{13.3mol}{1.66875mol} = 8$	$\frac{1.66875mol}{1.66875mol} = 1$

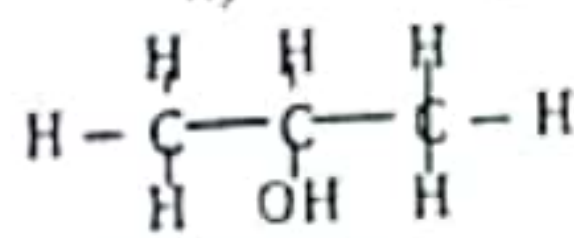
Hence empirical formula is C_3H_8O Let molecular formula of the compound be $(C_3H_8O)_n = C_{3n}H_{8n}O_n$ Then $36n + 8n + 16n = M_r = 60$ $60n = 60$ or $n = 1$ Hence molecular formula of A is C_3H_8O .

(i) Isomers of A are

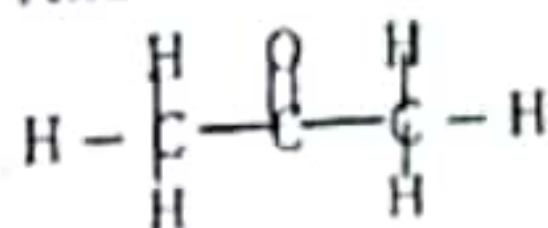


b)

- Since B is not carboxylic acid and resist further oxidation by Fehling's solution it must be ketone
 - Hence the class of compound to which B belong is ketone
- The alcohol which gives ketone on oxidation is secondary alcohol.
 - Hence the structure of A is

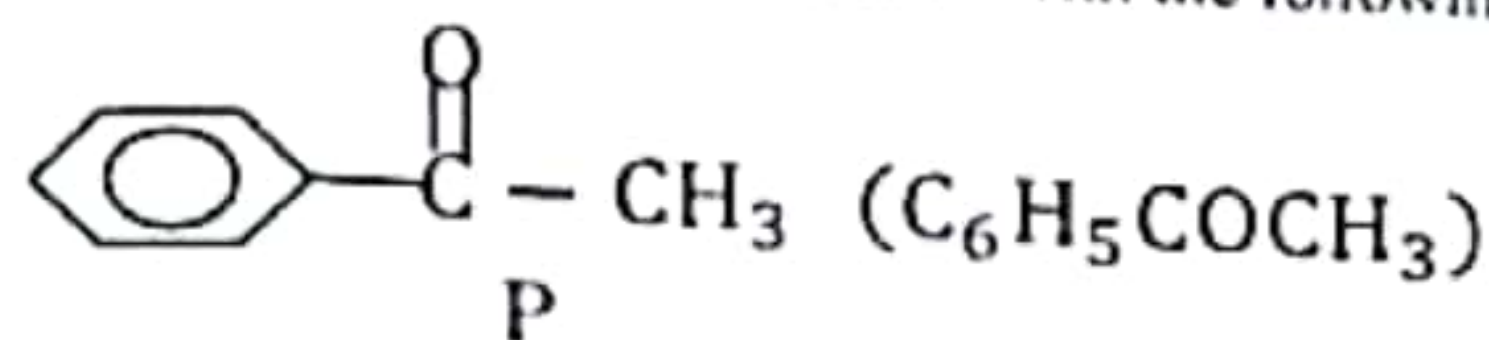


And that of B is

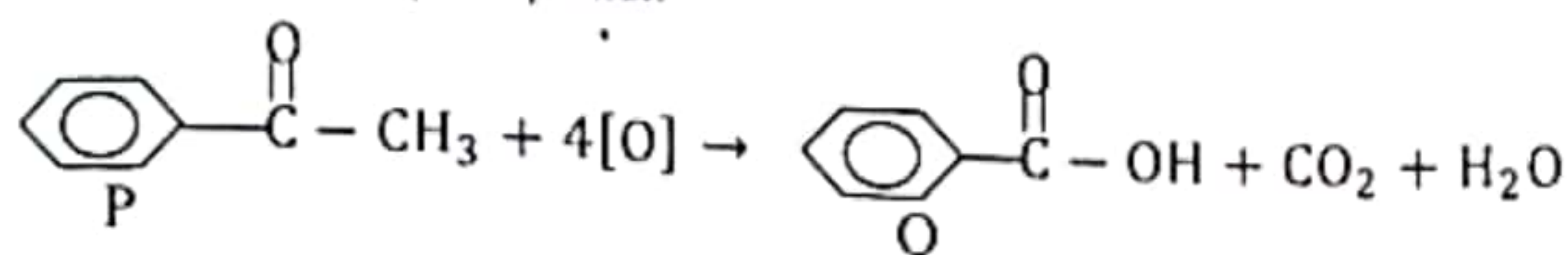


Question 61

- The molecule formula C_8H_8O confirm the general molecular formula of $C_nH_{2n-8}O$.
Thus with 8 carbon, P may be aromatic aldehyde or ketone
- Since P give iodoform reaction there is terminal methyl group bonded to carbonyl group in P. (P contains $-CO-CH_3$ group).
Therefore P must be aromatic ketone with the following structure;

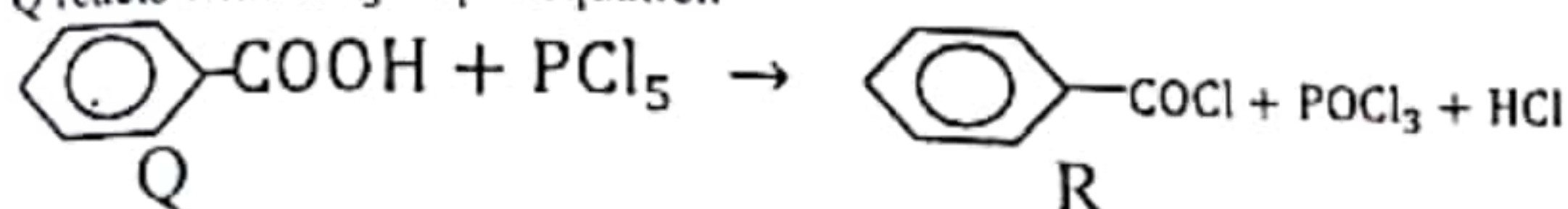


- P undergo vigorous oxidation as per equation

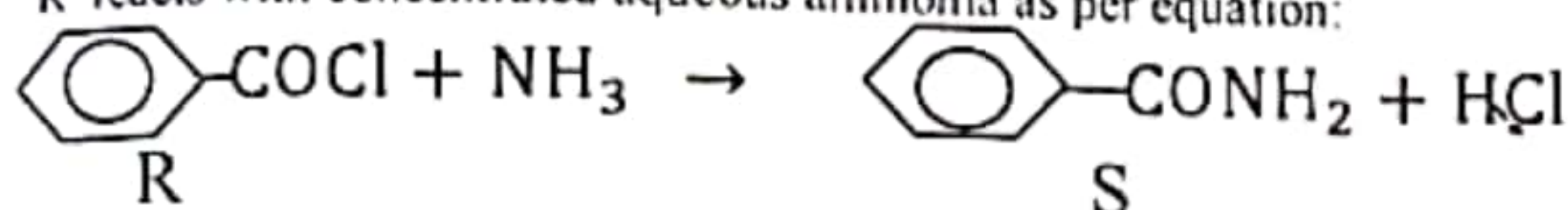


Formation of buff coloured when Q is treated with FeCl_3 confirm that Q is carboxylic acid as indicated above

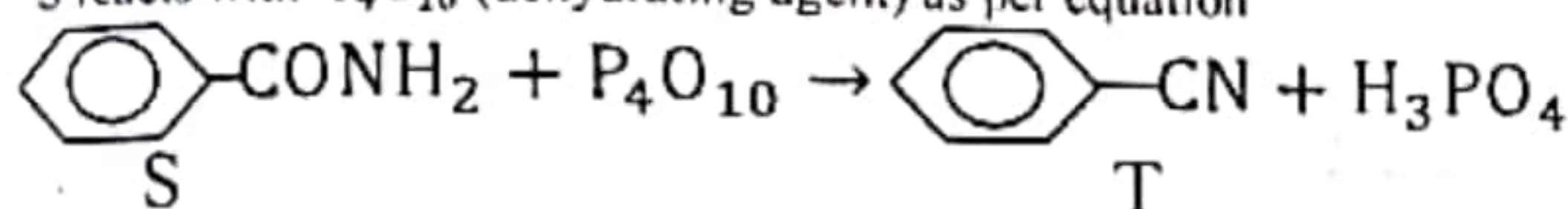
- Q reacts with PCl_5 as per equation



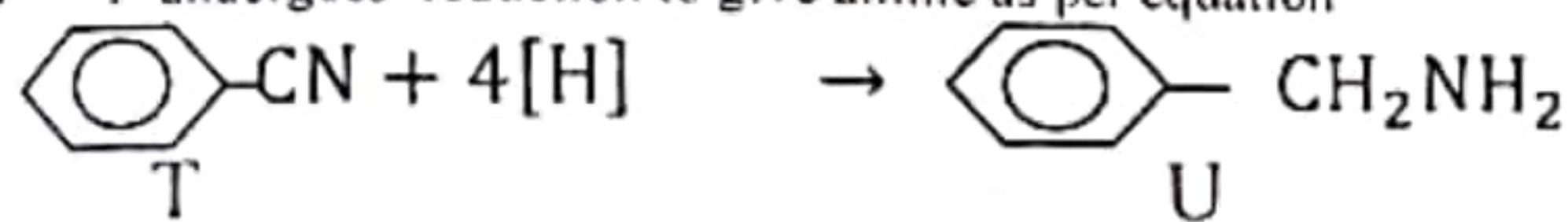
- R reacts with concentrated aqueous ammonia as per equation:



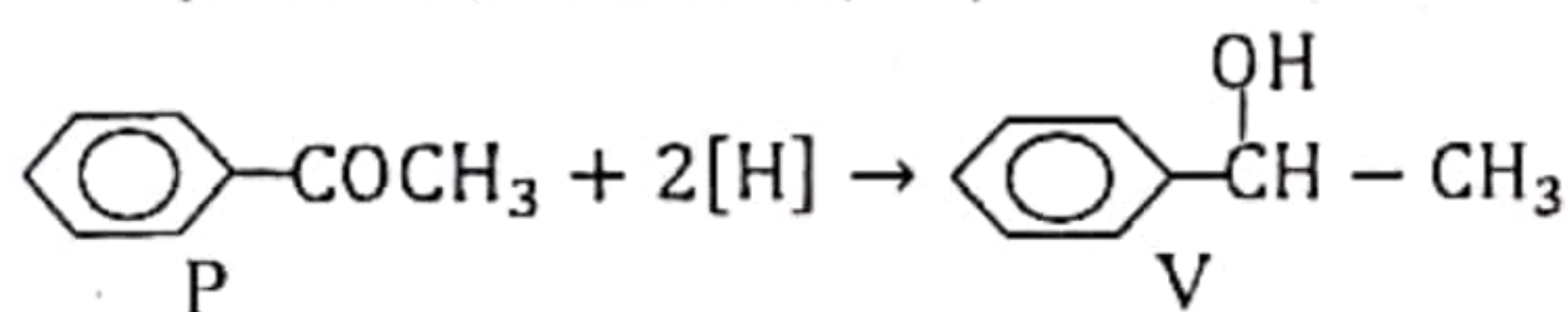
- S reacts with P_4O_{10} (dehydrating agent) as per equation



- T undergoes reduction to give amine as per equation

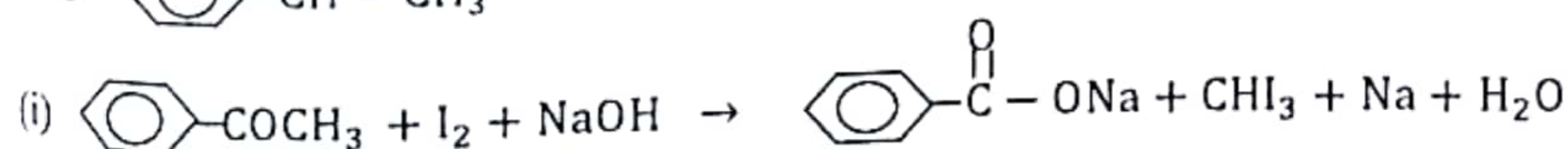
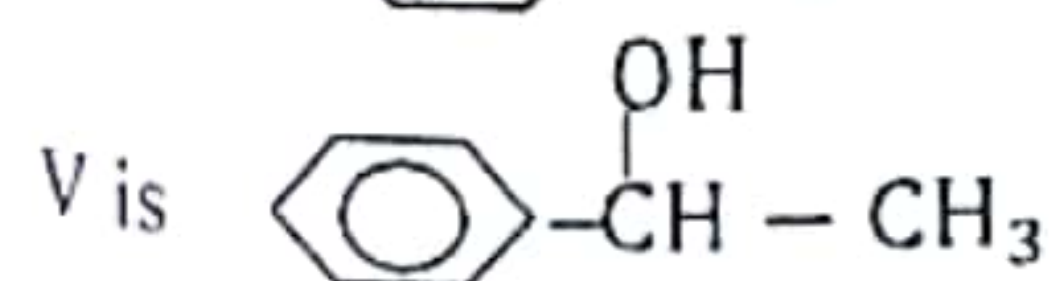
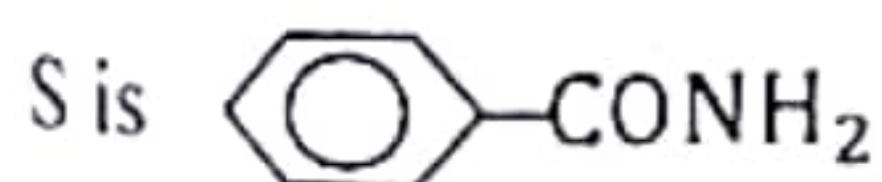
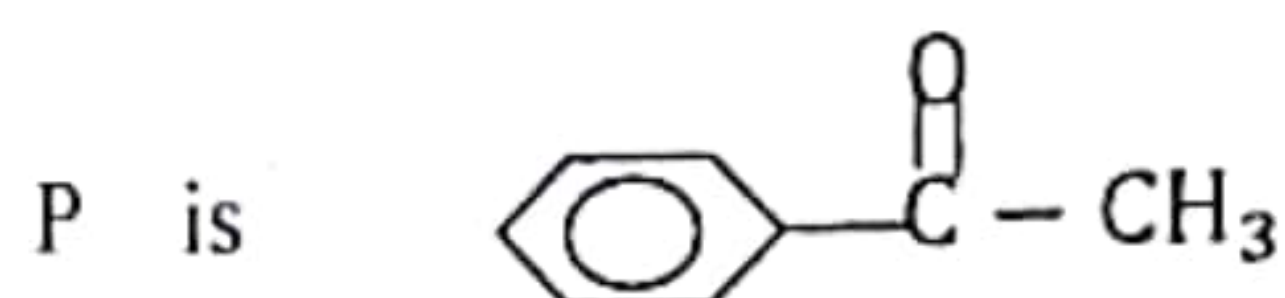


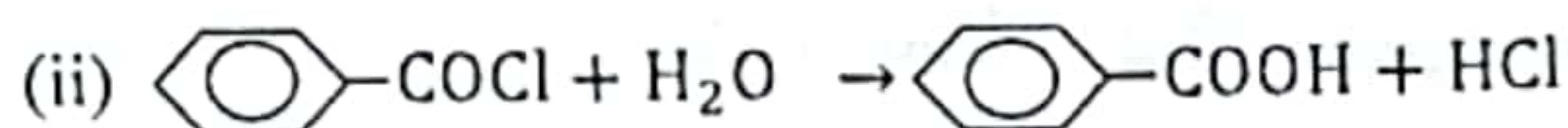
- P may also undergo reduction as per equation



Where $[\text{H}]$ stand for nascent hydrogen from mixture of concentrated HCl and sodium amalgam

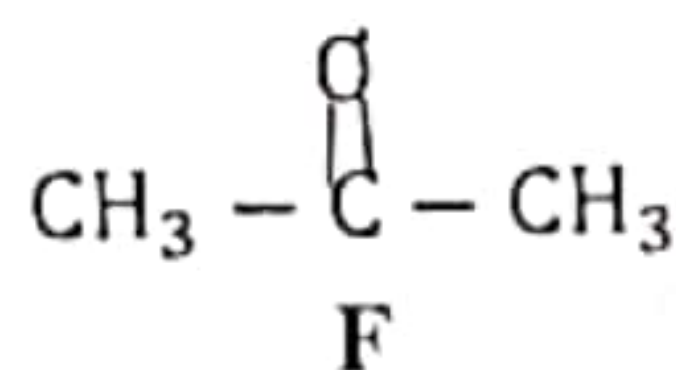
a)





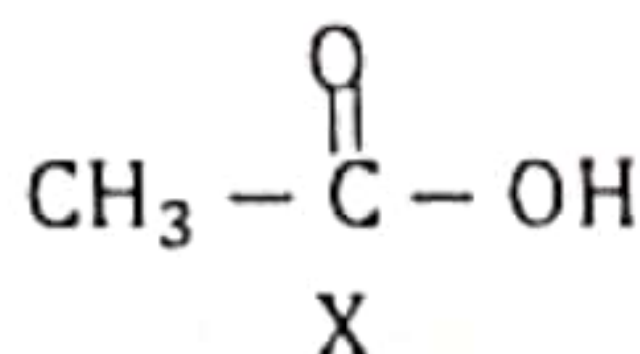
Question 62

- The molecular formula $\text{C}_3\text{H}_6\text{O}$ confirm the general molecular formula of $\text{C}_n\text{H}_{2n}\text{O}$.
- Thus F may be carbonyl compound or unsaturated alcohol with $\text{C}=\text{C}$
- Since F does not undergo oxidation (in presence of Fehling's solution and Tollen's reagent) and form 2,4-dinitrophenylhydrazone (which confirm that there is carbonyl group in F) it cannot be either unsaturated alcohol or aldehyde. It must be ketone of the following structure.



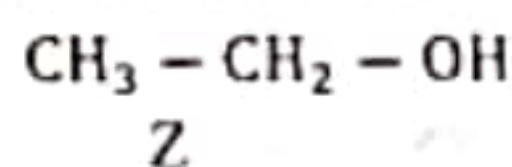
(Note with 3 carbons there is only one isomer of ketone)

- A compound which gives CH_3COCH_3 upon heating with $\text{Ca}(\text{OH})_2$ is ethanoic acid
- So X must be carboxylic acid with the following structure:-

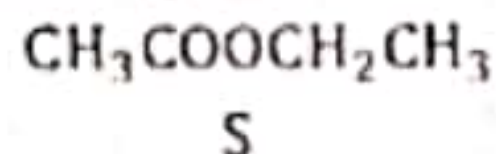


(Note: with 3 carbons, there is only one isomer of ketone)

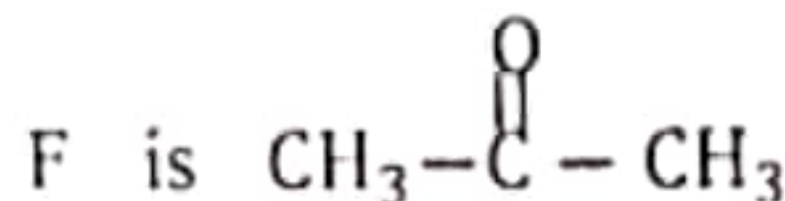
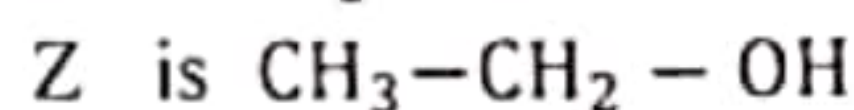
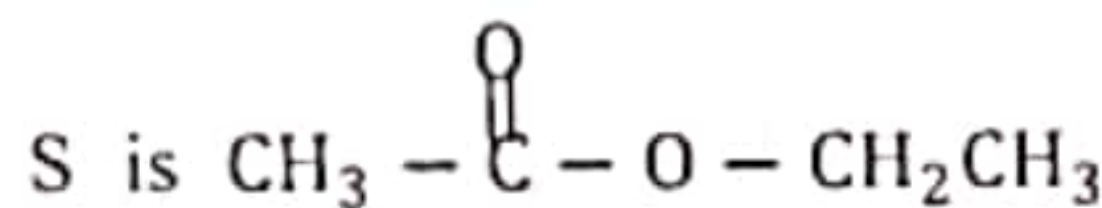
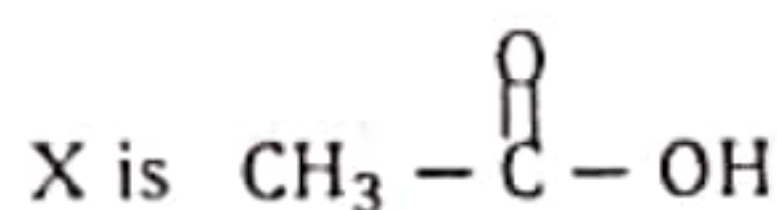
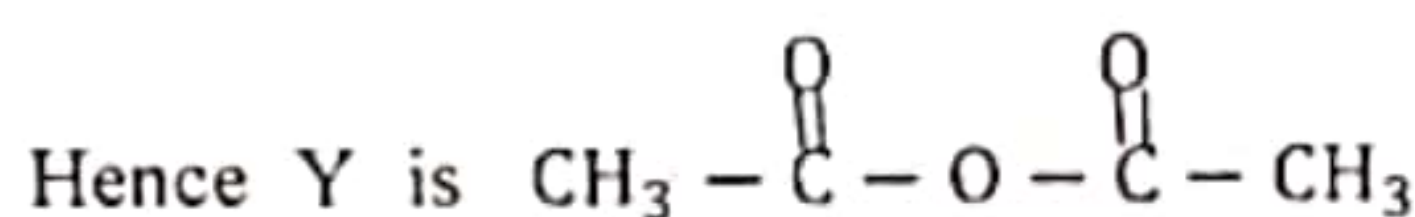
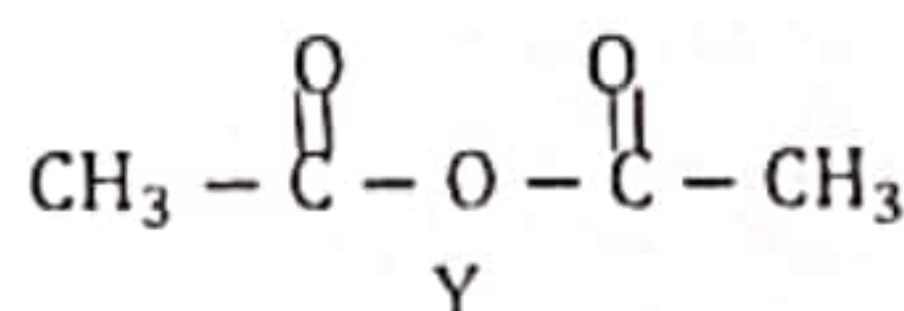
- Compound which gives carboxylic acid in oxidation is either aldehyde or alcohol.
- So Z may be either aldehyde or alcohol
- But Z is prepared by hydrolysis, the method which cannot be used to prepared aldehyde.
- So Z must be alcohol of the following structure:



- So the compound which gives X and Z on hydrolysis is the ester of the following structure:

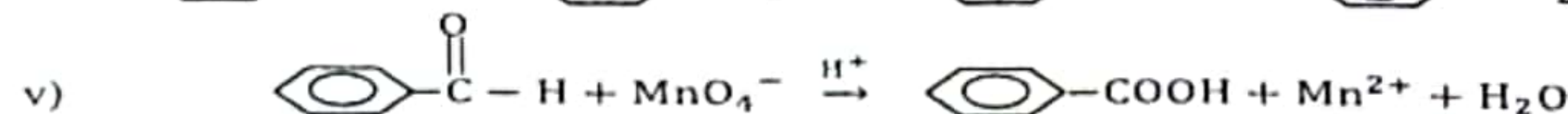
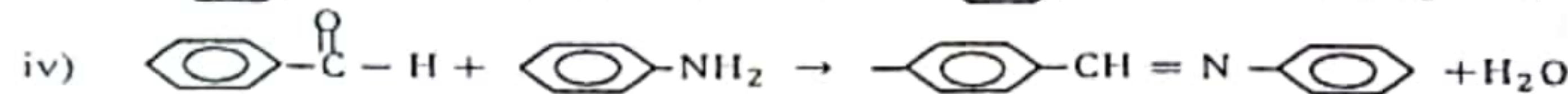
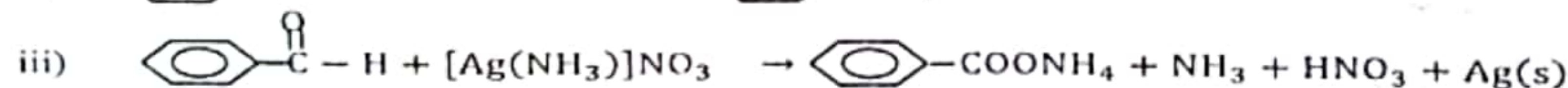
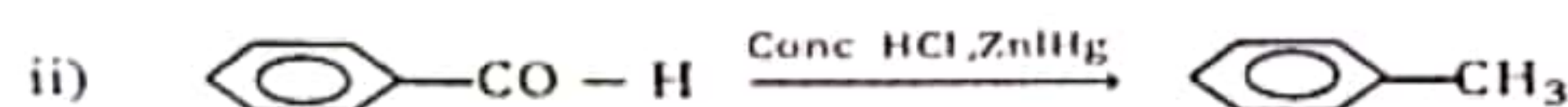
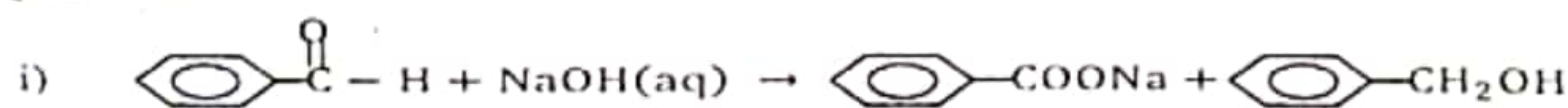


- A compound which gives ester (S) and carboxylic acid on treatment with alcohol (ethyl alcohol) is acid anhydride.
- Thus compound 'Y' is an acid hydride of the following structure:

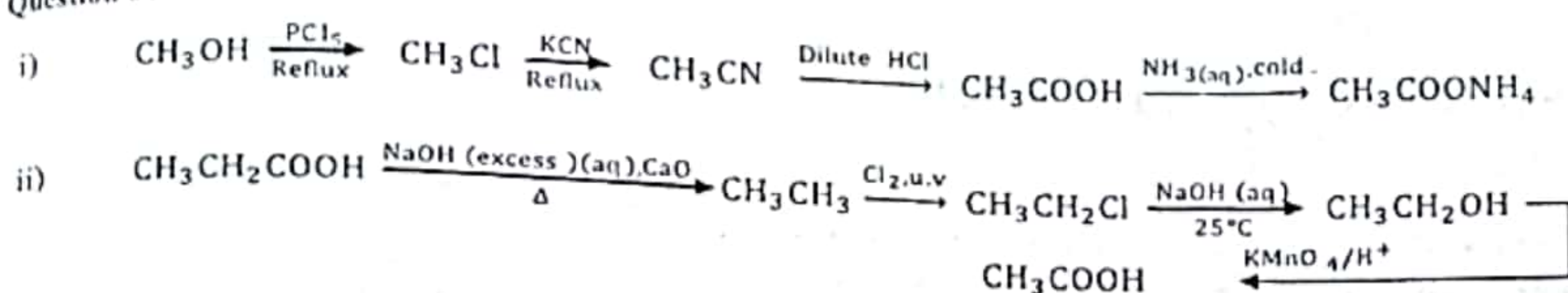


(On your own write all reactions involved- it more than easy for you!)

Question 63



Question 64



Question 65

B is $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$

Q is $\text{CH}_3\text{CH}_2\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$ or $\text{CH}_3\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$

And therefore A is $\text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH} = \overset{\text{CH}_3}{\text{C}} - \text{CH}_2\text{CH}_3$

D is CH_3COOH

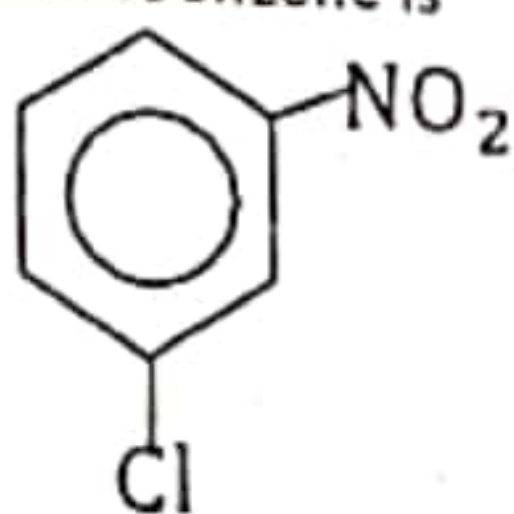
R is CH_3COCl

(On your own give IUPAC names for each compound)

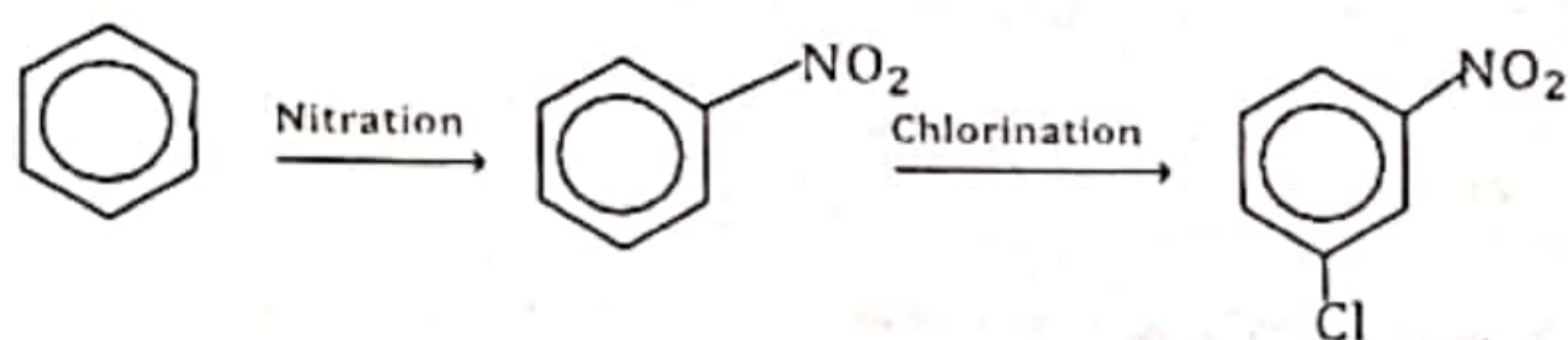
Question 66

a)

(i) The structure of 3-chloronitrobenzene is

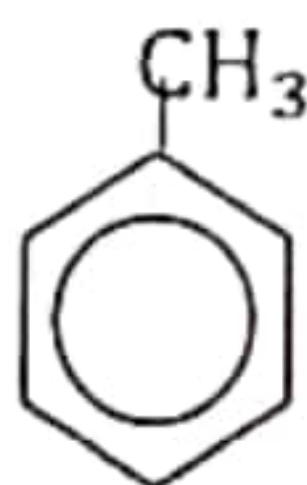


From which NO_2 and Cl are meta related and therefore NO_2 (meta director) must be entered first. Hence the sequence is nitration followed by chlorination.

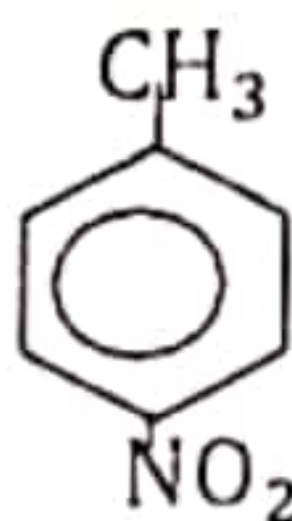


b)

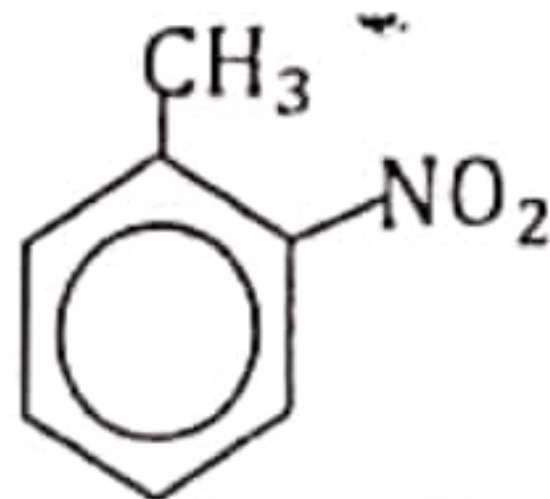
• A is



• B is



• C is



• D is

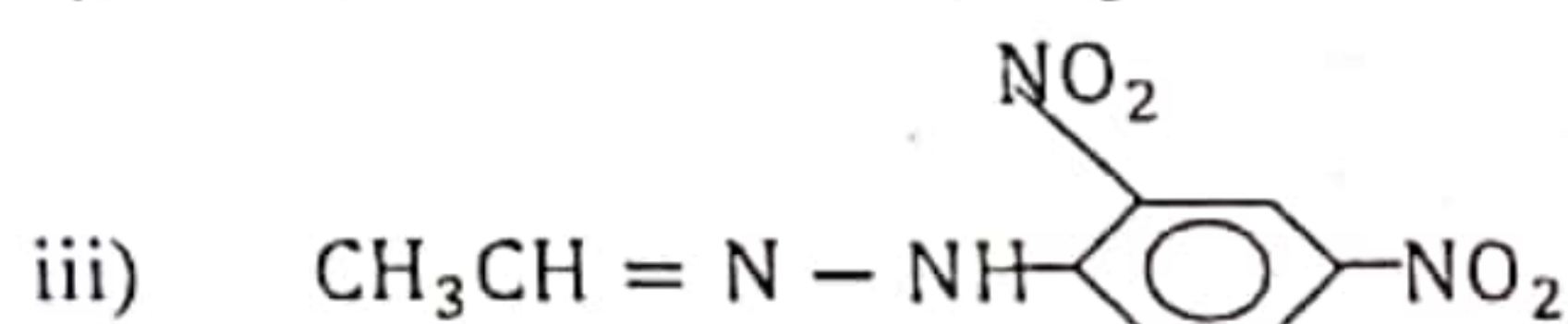
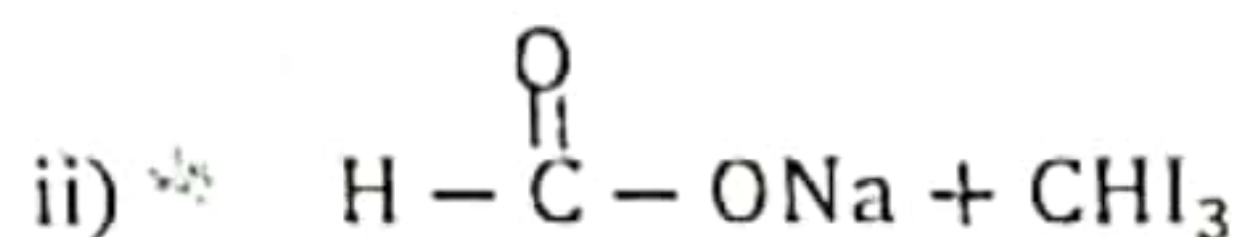
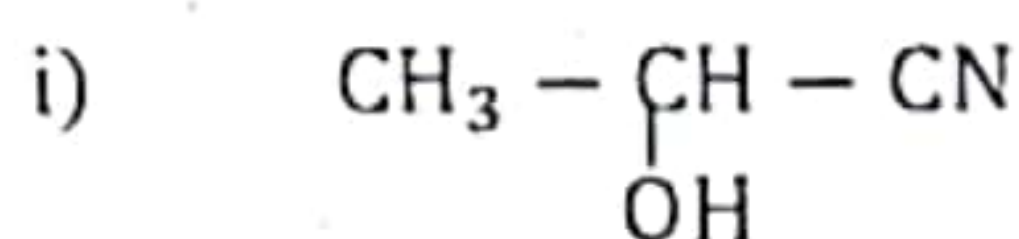


- E is $\text{CH} \equiv \text{CH}$

- F is $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$

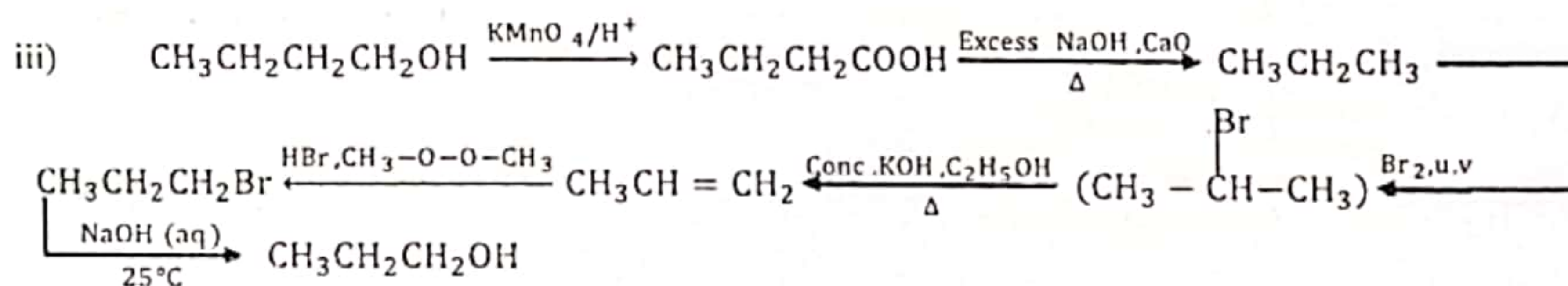
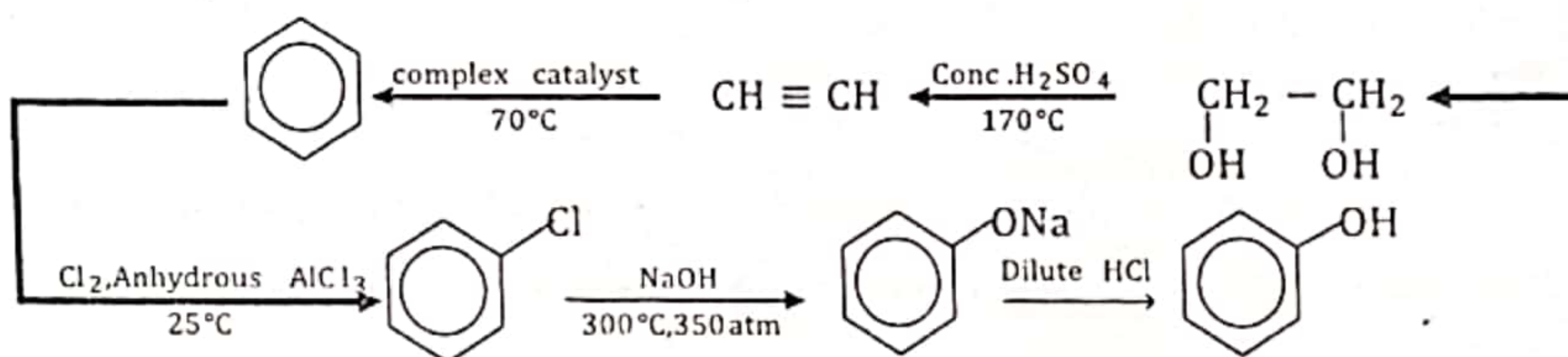
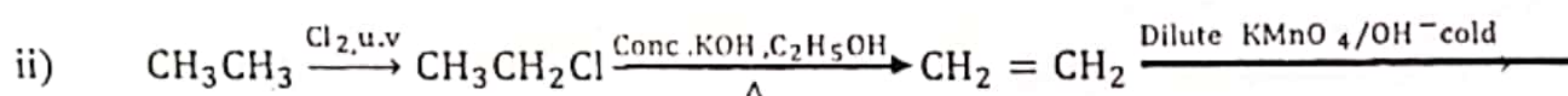
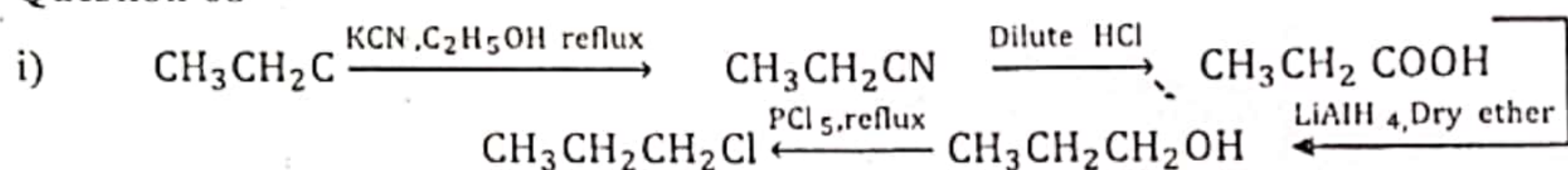
- G is $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- H is $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- I is $\text{CH}_3\text{CH}_2\text{COOH}$

Question 67



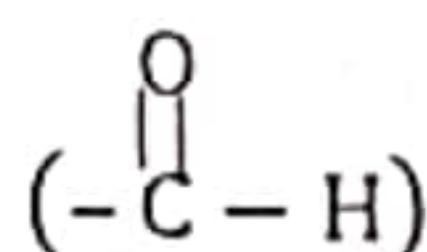
(When you are asked to write structure of product(s), it is important to write structure of organic product(s) only.)

Question 68

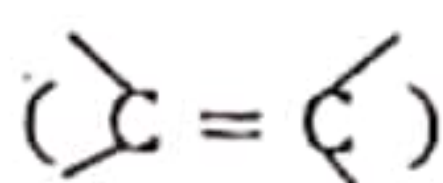


Question 69

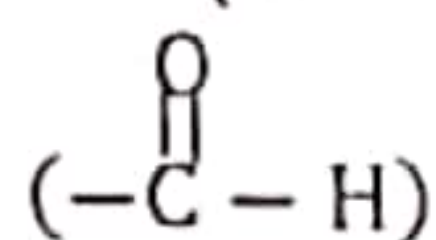
- i) Aldehyde (or carbonyl) group



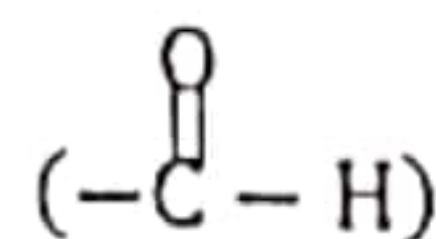
- ii) Alkene group



- iii) Aldehyde group



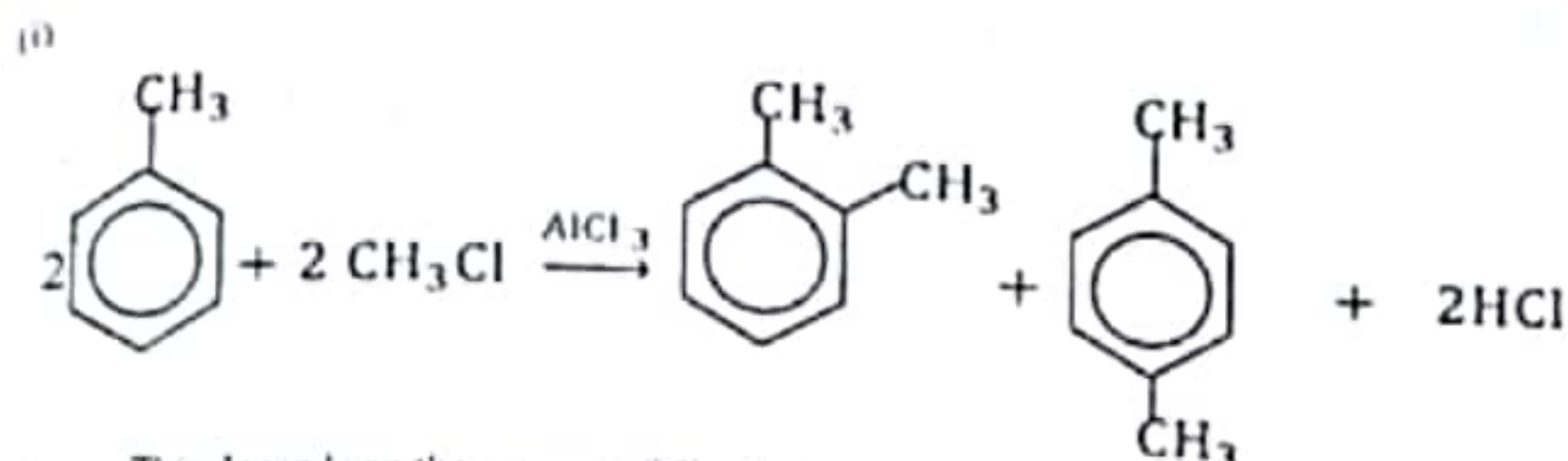
- iv) Aldehyde group



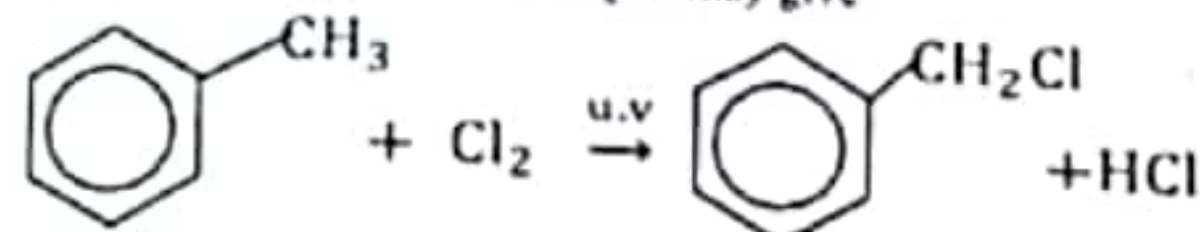
- v) Benzene ring (or phenyl group),



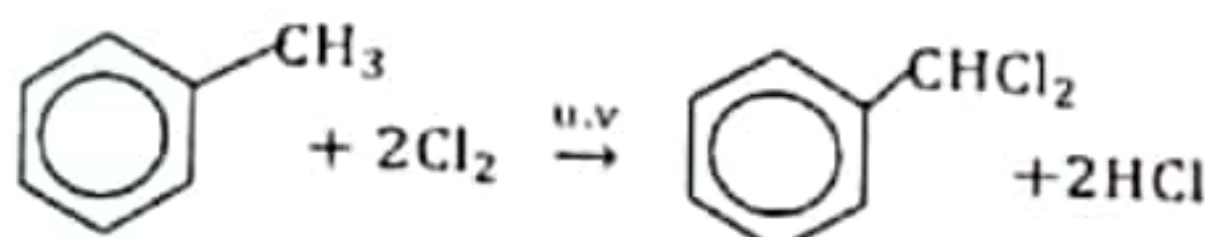
Question 70



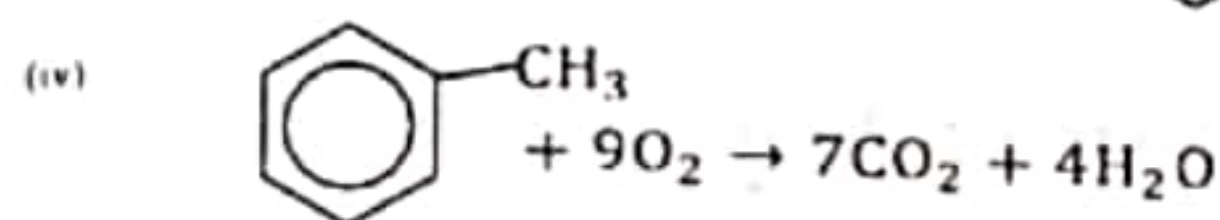
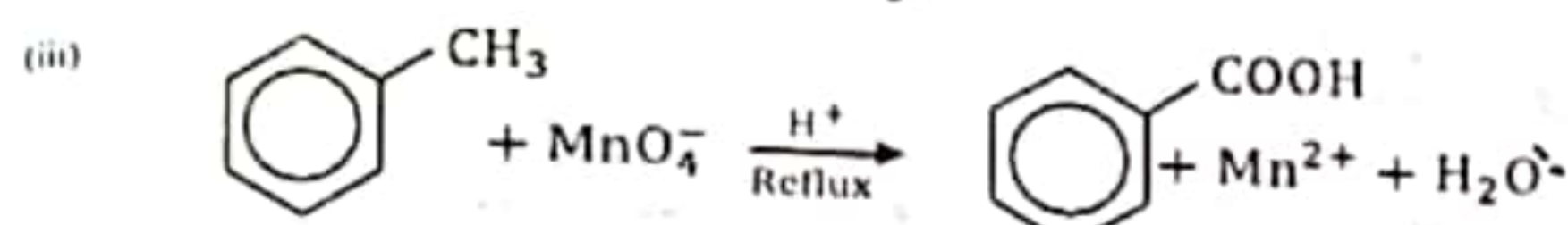
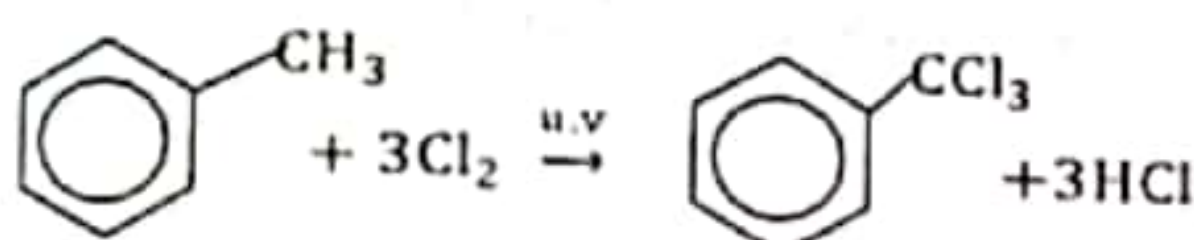
(ii) This depends on the amount of Cl_2 . It may give



Or



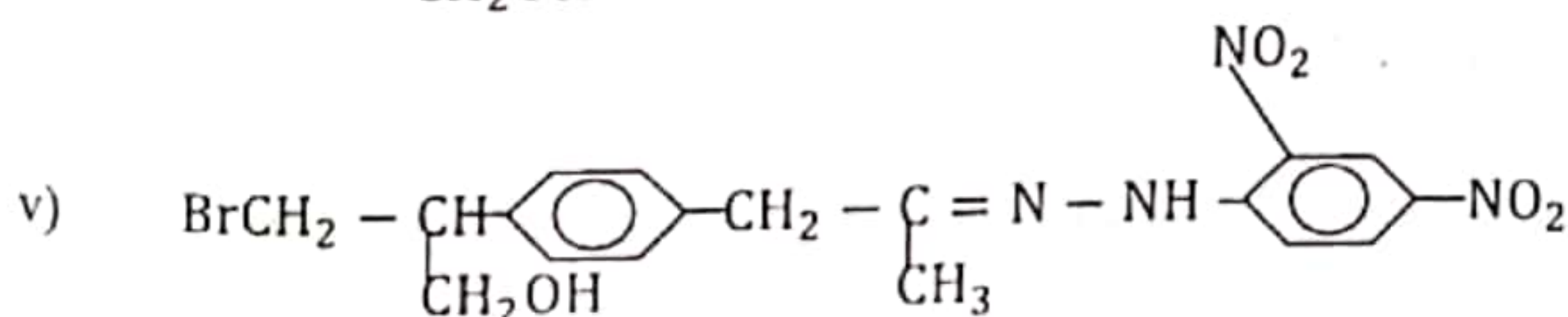
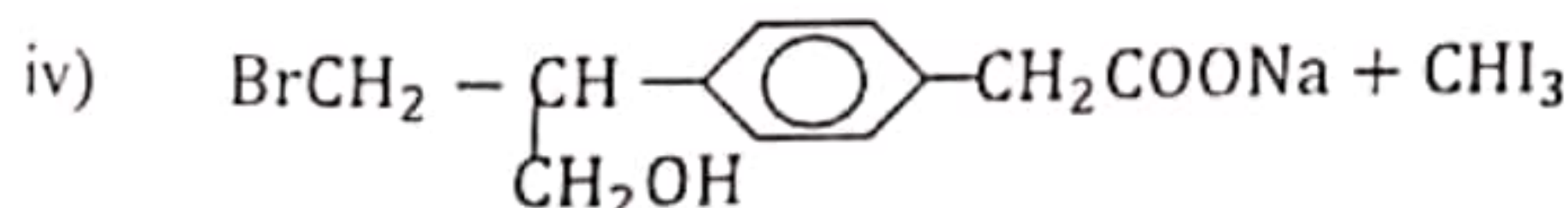
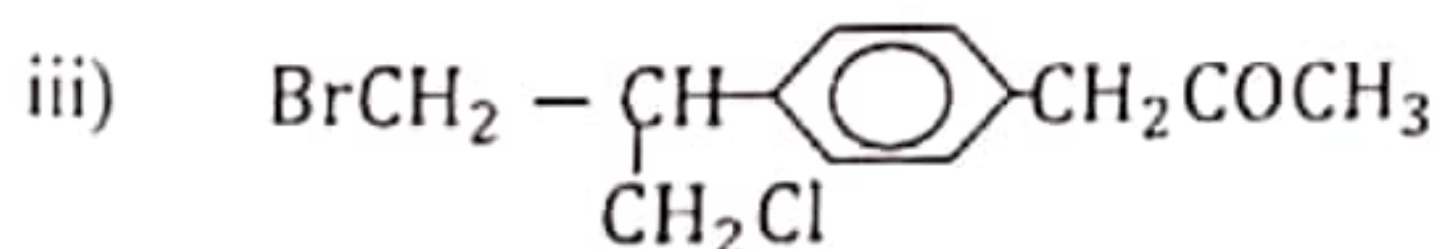
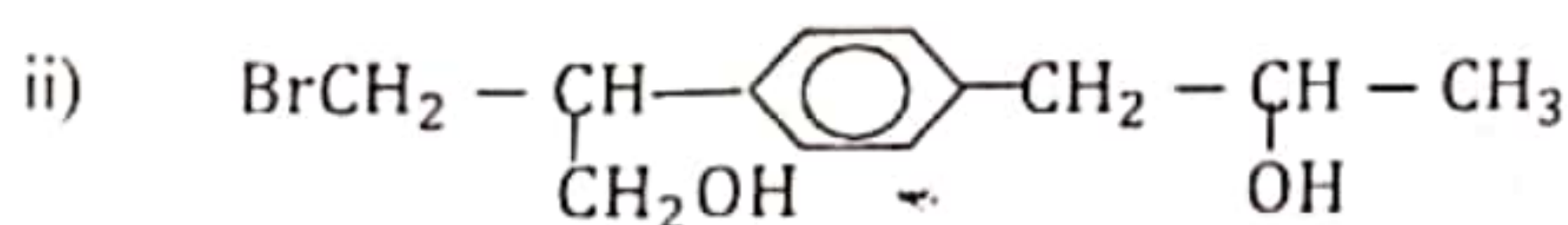
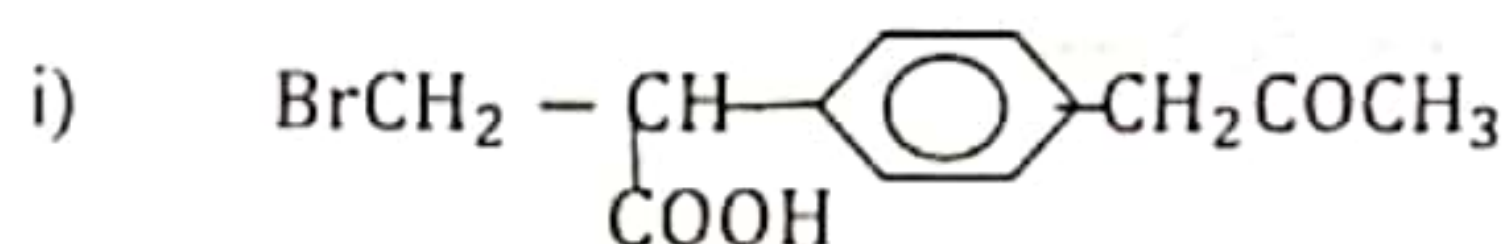
Or



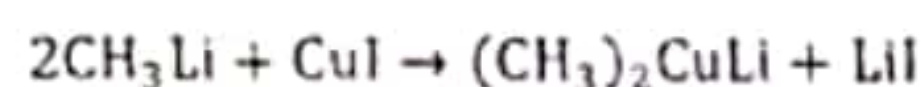
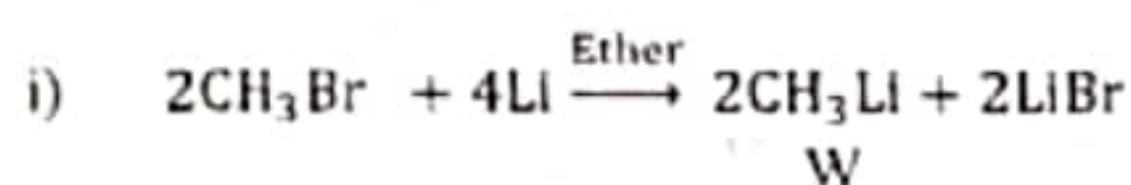
Question 71

- i) Refer to the text
- ii) Carbonyl group ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$)
- iii)
- They have stronger positive inductive effect accompanied by stronger steric hindrance from two alkyl (or aryl) groups.
 - This makes ketones less reactive toward nucleophiles in nucleophilic addition reaction which is the characteristic reaction of carbonyl compounds.
 - They have no replaceable hydrogen atom in the carbonyl group.
 - This makes ketone to resist oxidation reaction unlike aldehydes which undergo oxidation reaction readily because they have replaceable hydrogen in $-\text{CO}-\text{H}$ (Aldehyde group).

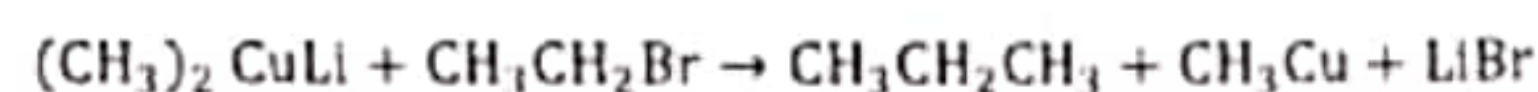
Question 72



Question 73



W



2

Y

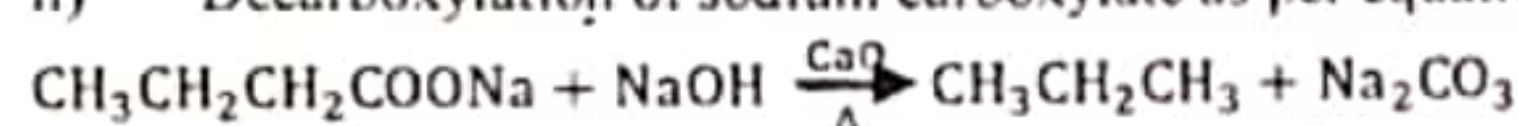
Therefore:

W is: CH_3Li Name: methyl lithium

Z is : $(\text{CH}_3)_2\text{CuLi}$ Name: lithium diethylcuprate

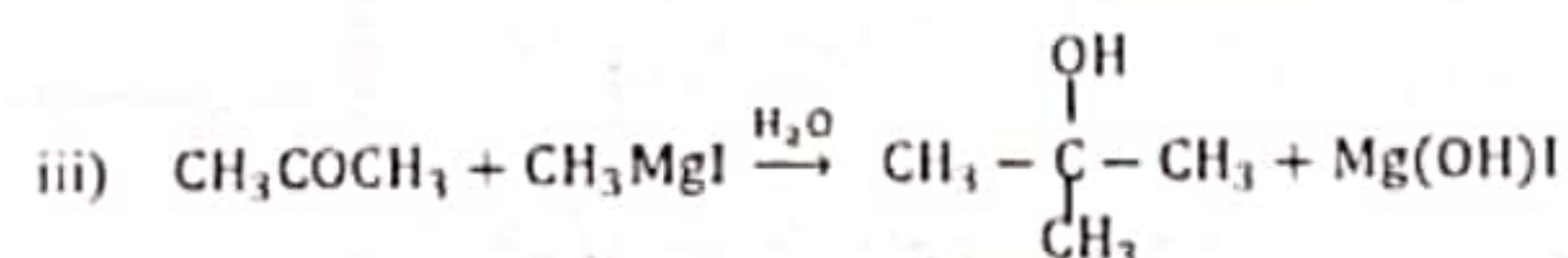
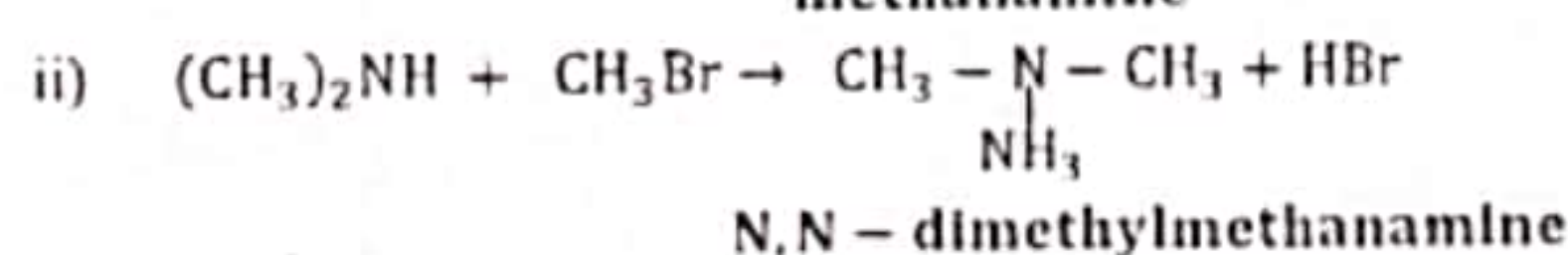
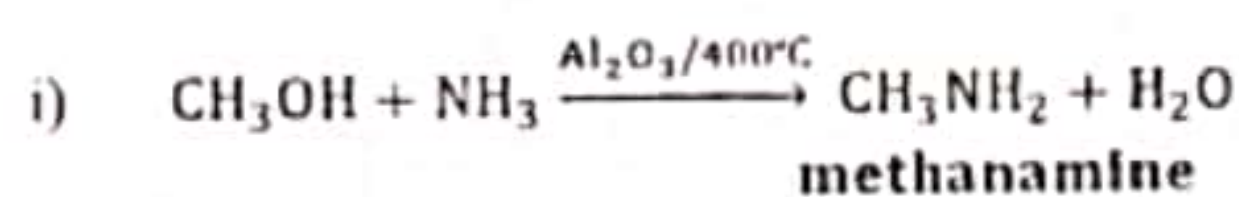
Y is : $\text{CH}_3\text{CH}_2\text{CH}_3$ Name: propane

ii) Decarboxylation of sodium carboxylate as per equation (or any other correct method)



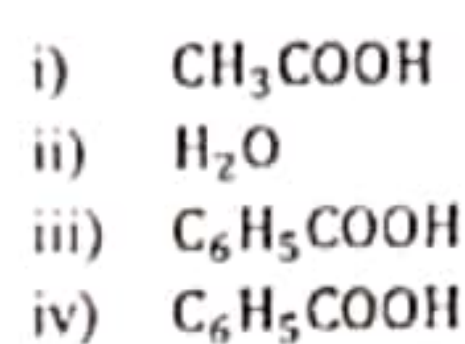
Question 74

a)



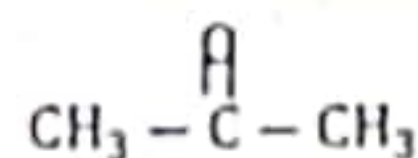
2 - Methylpropan - 2 - ol

b)

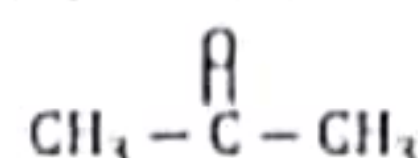


Question 75

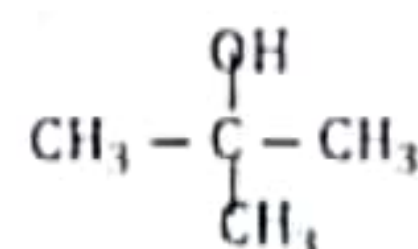
- The molecular formula C_3H_6O , confirm the general molecular formula of $C_nH_{2n}O$
- Thus the given compound may be unsaturated alcohol with $C=C$ or carbonyl compound
- Since the compound gives alcohol with Grignard reagent followed by hydrolysis, it cannot be alcohol it must be carbonyl compound, that is aldehyde or ketone
- Since the alcohol formed resist oxidation reaction it must be tertiary alcohol
- The carbonyl compound which gives tertiary alcohol on the reaction with Grignard reagent followed by hydrolysis is ketone. Hence the given compound cannot be aldehyde, it must be ketone of the following structure



Hence the structure of the original compound is



And the structure of alcohol is



Question 76

i) Λ

Reason:

Hint: Cl is more electronegative and therefore exerts stronger negative inductive effect.

ii) D
Reason

Hints: is closer to COOH group and therefore stronger negative inductive experience by the carboxylic group in D

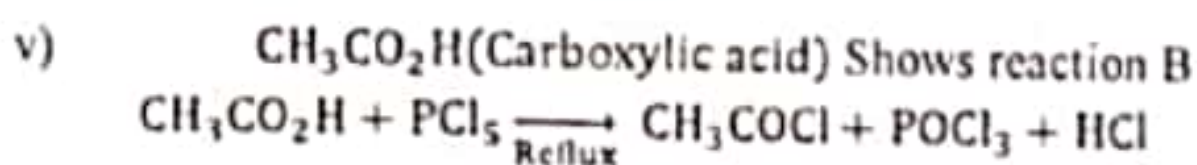
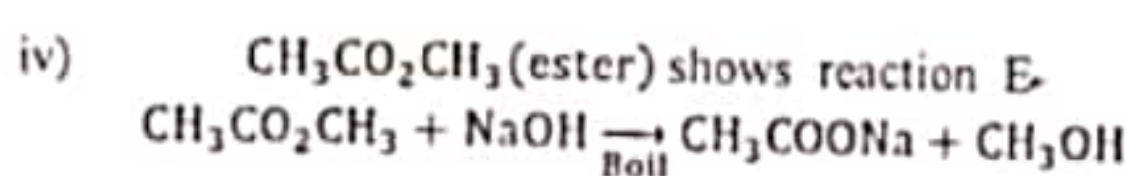
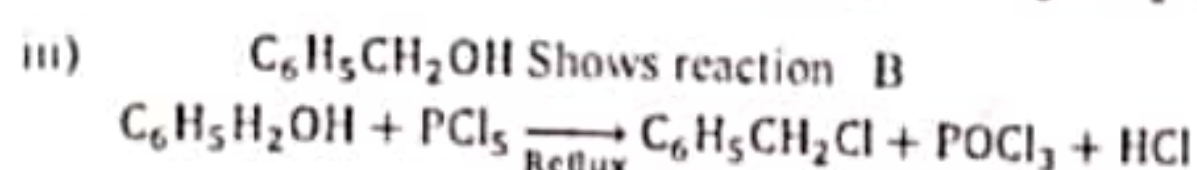
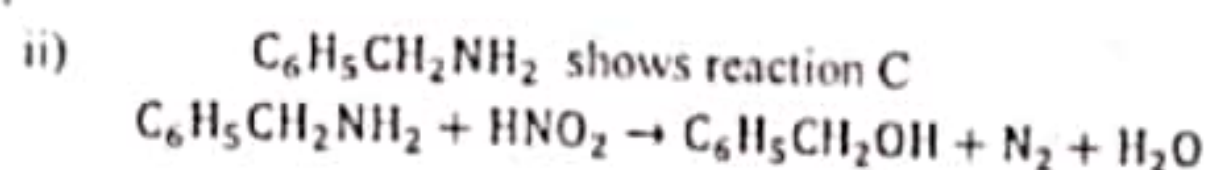
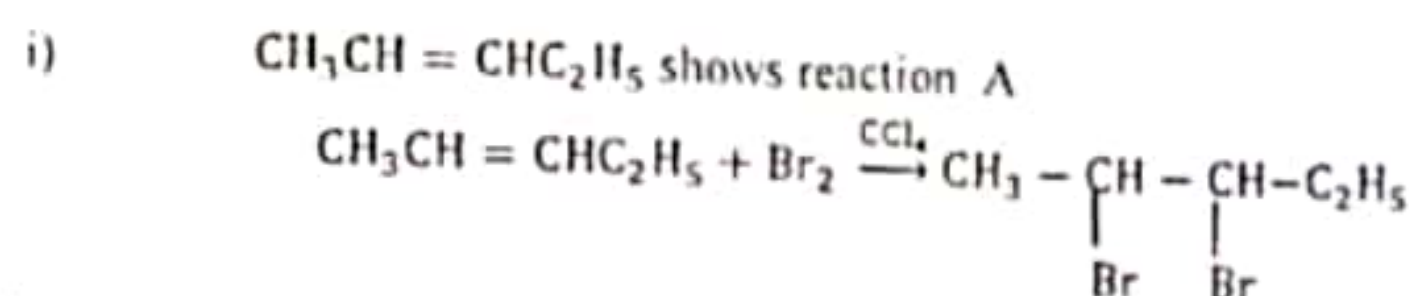
iii) F
Reason

Hint: NO₂ group is deactivator

iv) G
Reason

Hint: the carboxylate ion in G is stabilised by intra-hydrogen binding

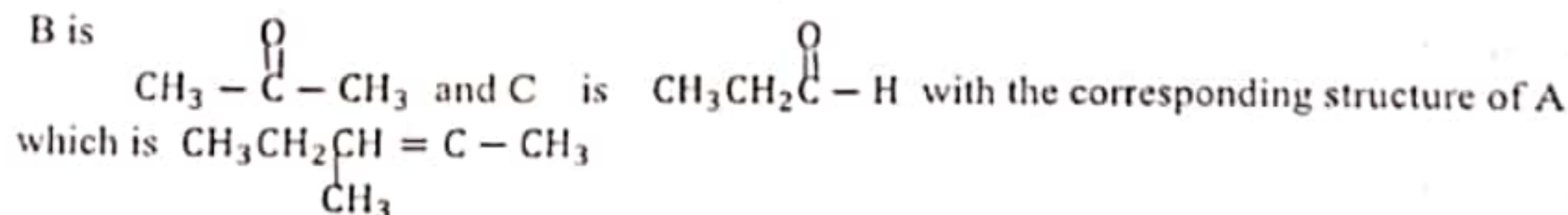
Question 77



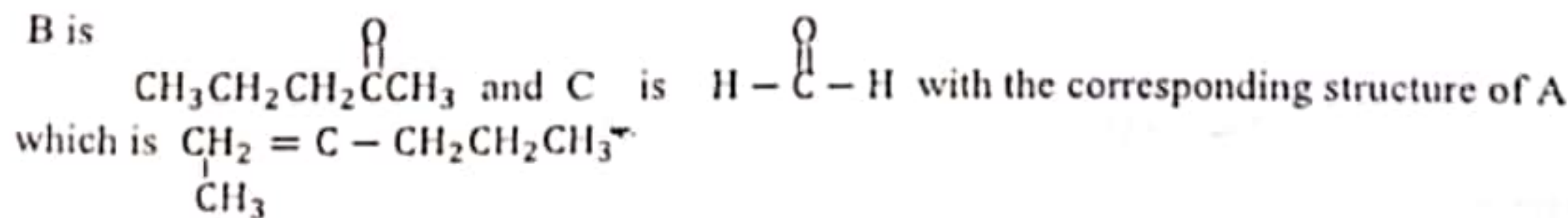
Question 78

- Since B and C give yellow – orange precipitate with Brady's reagent they must be carbonyl compounds.
- Since B gives positive triiodomethane test, there must terminal methyl group bonded to carbonyl group in the compound; that is –CO – CH₃ group in B and there is no such group in C because it gives negative test.
- Since C gives positive mirror test, it must be aldehyde.
- So C is the aldehyde without terminal methyl group to carbonyl group.
- Since B does not give positive mirror test, it must be ketone.
- So B is methyl ketone

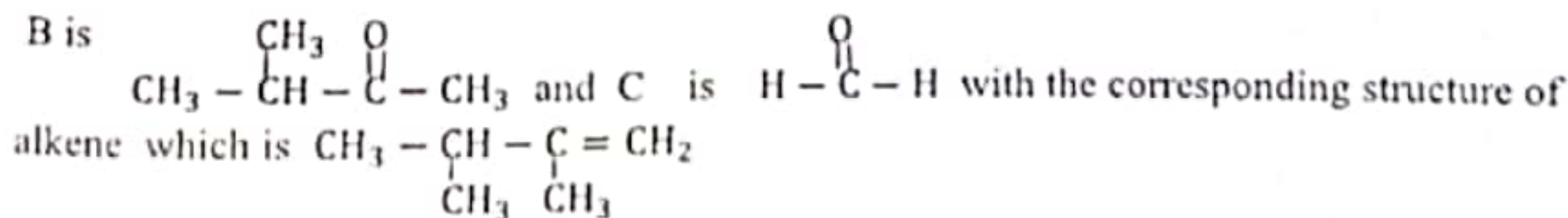
Hence either:



Or



Or



(Note: B cannot be ketone with 4 carbons because this would give CH₃CO – H (Ethanal) on the aldehyde side which would give positive triiodomethane test which is the opposite fact of the given information of the question)

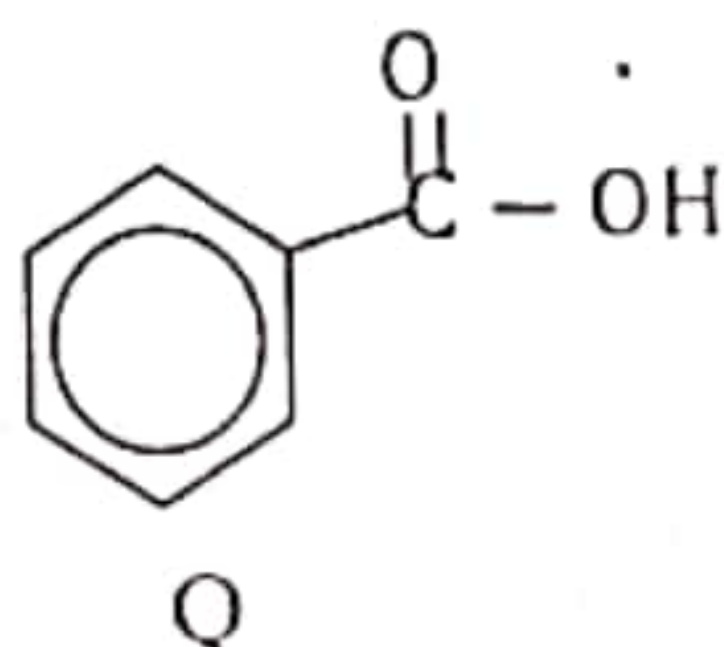
Question 79

- The general molecule formula of ester is either C_nH_{2n}O₂ (for aliphatic ester) or C_nH_{2n-8}O₂ (For aromatic ester) where n must be whole number.
- For aliphatic ester (C_nH_{2n}O₂):

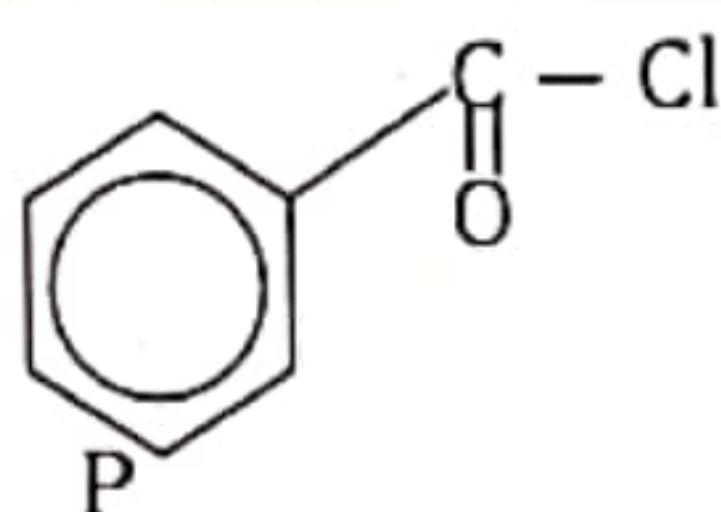
$$12n + 2n + 32 = 150; n = 8.43. \text{ (Not whole number)}$$

Thus the ester cannot be aliphatic

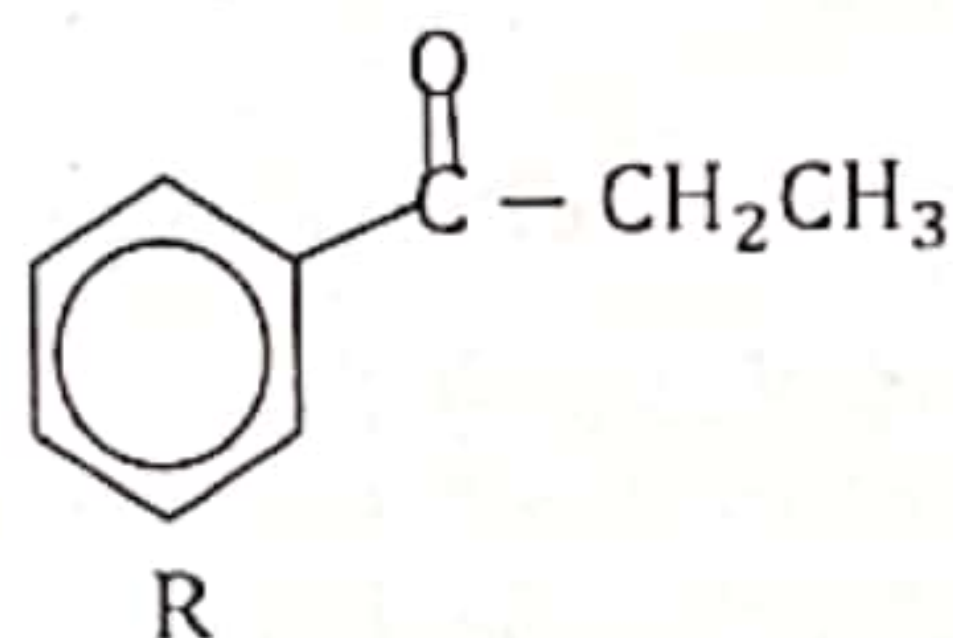
- For aromatic ester ($C_nH_{2n-8}O_2$)
 $12n + 2n - 8 + 32 = 150$; $n = 9$ (Whole number)
- Thus the ester is aromatic with 9 carbons
Hence R is the aromatic ester with molecular formula of $C_9H_{10}O_2$
- Since R is produced from the reaction between monobasic acid and ethanol
- Q is aromatic carboxylic acid with 7 carbons of molecular formula of $C_7H_6O_2$ (The other two carbons in ester come from ethanol C_2H_5OH)
- Since there is only one isomer of aromatic carboxylic acid with 7 carbons the correct structure of Q is



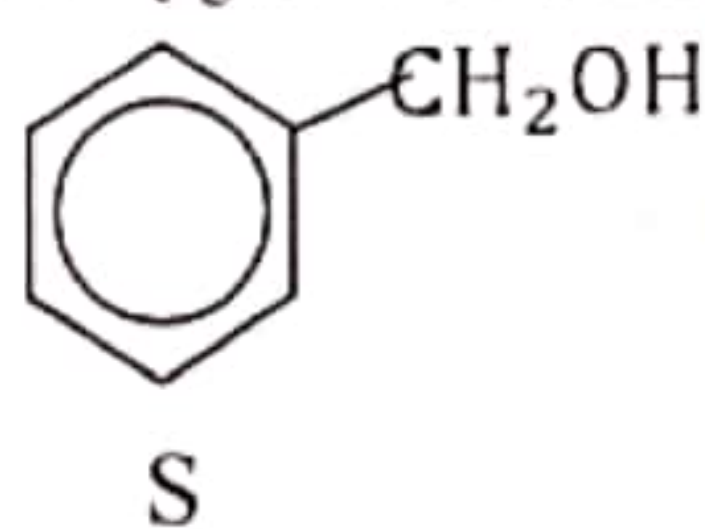
- The compound which gives carboxylic acid upon hydrolysis is acid halide
- Thus P is the acid halide of the following structure:



- Esterification of Q with ethanol gives the following ester which is R



- Reduction of Q gives the following alcohol which is S



Question 80

a)

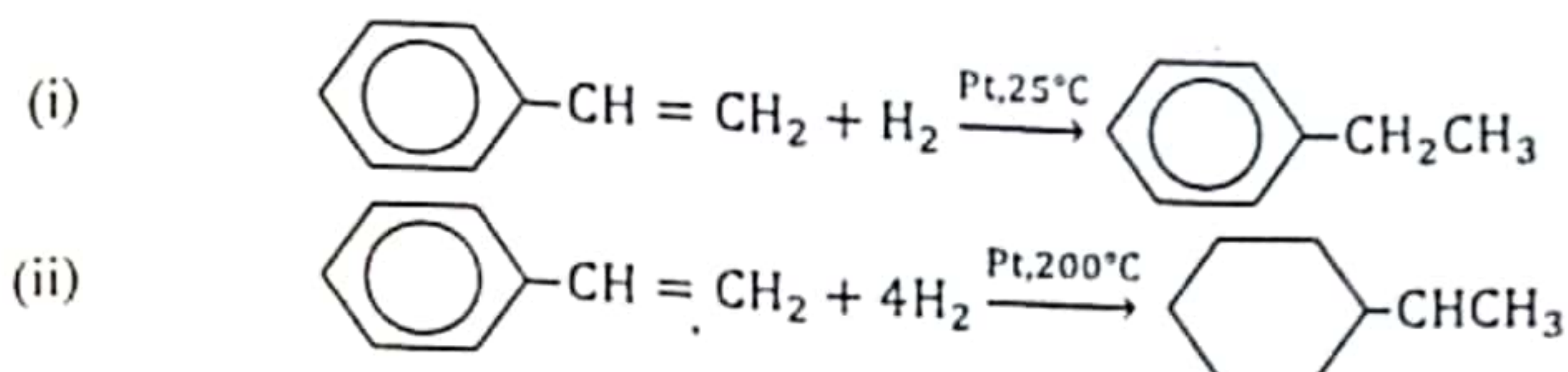
- $CH_3CH_2CHBrCH_3 \xrightarrow{\text{Aqueous KOH}} CH_3CH_2CH(OH)CH_3 + KBr$
- $CH_3CH_2CHBrCH_3 \xrightarrow{\text{Alcoholic KOH}} CH_3CH=CHCH_3 + KBr + H_2O$
- $2CH_3CH_2OH \xrightarrow[140^\circ C]{\text{Limited conc. } H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$
- $2CH_3CH_2OH \xrightarrow[170^\circ C]{\text{Excess conc. } H_2SO_4} 2CH_2=CH_2 + 2H_2O$
- $CH_3CH_2CH(OH)CH_3 \xrightarrow{\text{Excess conc. } H_2SO_4} CH_3CH=CHCH_3 + H_2O$

b) Hints:

- Use Lucas reagent (don't use iodoform test).
- Use Lucas test (or iodoform test)
- Use iodoform test
- Use alcoholic silver nitrate
- Use iodoform test

Question 81

Hydrogenation of unsaturated side chain of benzene requires lower temperature than that required for hydrogenation in benzene ring. At high temperature hydrogenation occurs in both side chain and benzene ring.

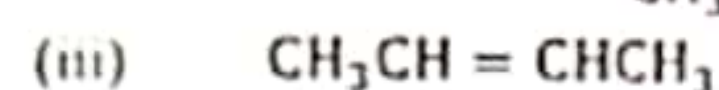
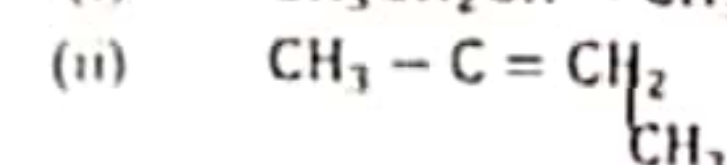
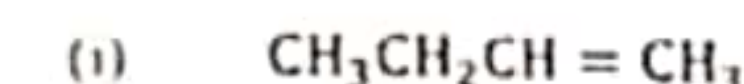


Will deactivate the benzene ring

(Any unsaturated group of hydrocarbon may act as deactivator if the carbon with double (or triple) bond is directly bonded to benzene).

Question 82

(c) Isomers of Y are



(d) Since Y gives only one product on ozonolysis, it must be symmetrical alkene

• But among mentioned isomer, symmetrical alkene is (iii) only.

• Hence Y is but-2-ene with the following structure $\text{CH}_3\text{CH}=\text{CHCH}_3$

Ozonolysis of but-2-ene followed by hydrolysis (in absence of zinc) gives ethanoic acid with the following structure: CH_3COOH

Note: Absence of zinc made the product to be carboxylic acid. In its presence the product becomes aldehyde (CH_3CHO)

Question 83

CaC_2 Reacts with H_2O to give ethyne according to the following equation: $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2$

From which mole ratio of CaC_2 to C_2H_2 is 1:1

From $PV = nRT$, $n = \frac{PV}{RT}$

Thus number of moles of C_2H_2 (ethyne) formed was;

$$n = \frac{1 \times 200 \times 10^{-3}}{0.082 \times 300} \text{ mol} = 8.13 \times 10^{-3} \text{ mol}$$

From the mole ratio of C_2H_2 to CaC_2 is 1:1.

Thus number of moles of CaC_2 was also $8.13 \times 10^{-3} \text{ mol}$

But molar mass of $\text{CaC}_2 = 64 \text{ g/mol}$

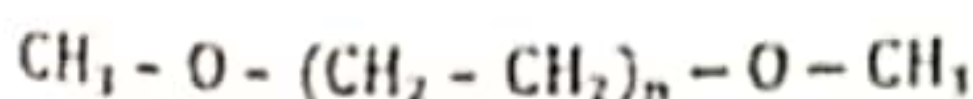
Whence mass of $\text{CaC}_2 = 8.13 \times 10^{-3} \text{ mol} \times 64 \text{ g/mol} = 0.52 \text{ g of } \text{CaC}_2 \text{ in } 0.64 \text{ g of its impure form}$

$$\text{Then } \% \text{ CaC}_2 = \frac{0.52}{0.64} \times 100\% = 81.25\%$$

Hence the percentage purity of calcium carbide is 81.25%

Question 84

With $\text{CH}_3-\text{O}-\text{O}-\text{CH}_3$ as initiator, from which CH_3O attach to polymer at initiation step and another CH_3O attach to the polymer at the termination step



Where n is the number of monomers

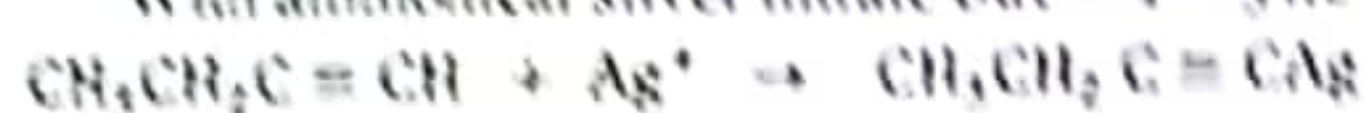
$$\text{Thus } 12 + (1 \times 3) + (16 \times 2) + 12 + (1 \times 3) + (12 + 2 + 12 + 2)n = 52926$$

$$28n = 52926 \text{ or } n = 1888$$

Hence number of monomer in the polymer is 1888

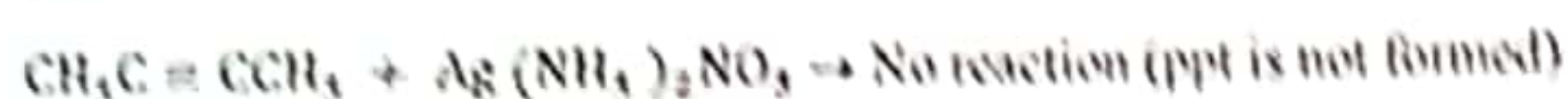
Question 85

- i. With ammonical silver nitrate but-1-yne gives white precipitate while but-2-yne does not i.e



(from $\text{Ag}(\text{NH}_3)_2\text{NO}_3$) White ppt

BUT

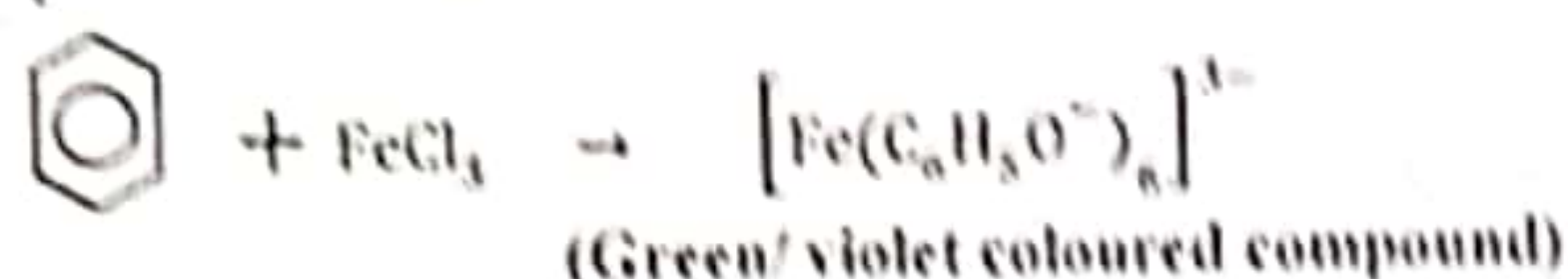
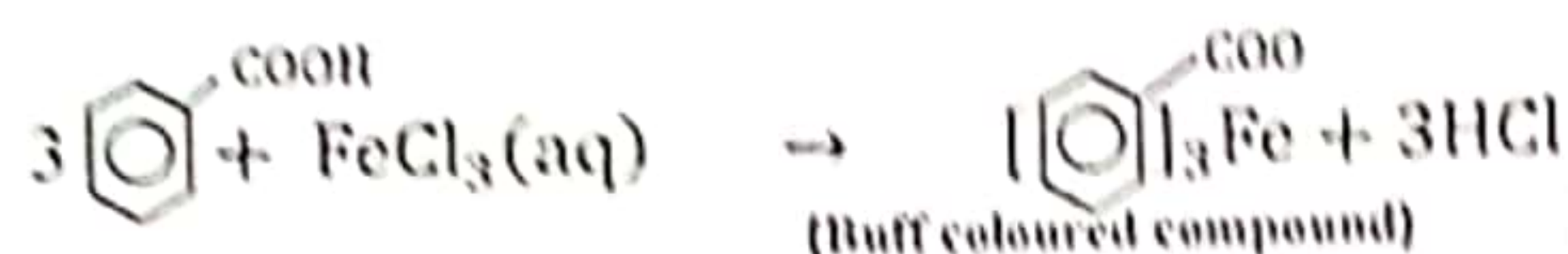


- ii. With solution of iron (III) chloride benzoic acid give buff coloured compound.

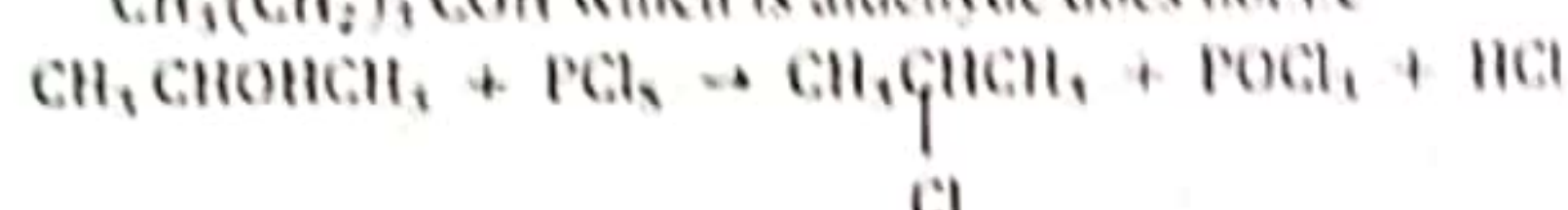
While

Phenol yield violet coloured compound

i.e

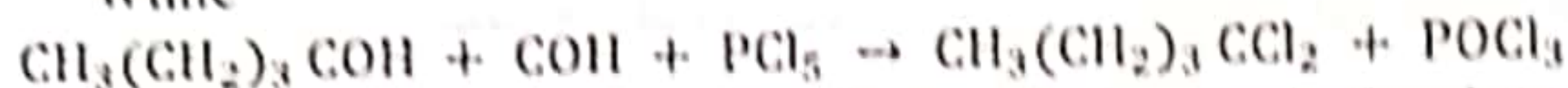


- iii. With phosphorous pentachloride $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ yield a gas which produced dense white fumes with aqueous ammonia while $\text{CH}_3(\text{CH}_2)_3\text{COH}$ which is aldehyde does not i.e



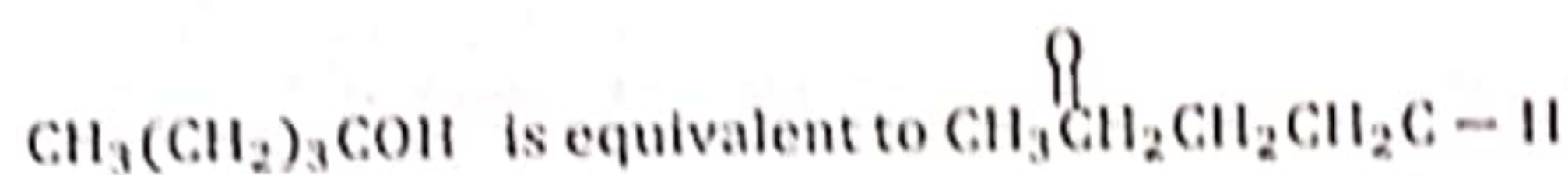
(HCl(g) produce dense white fumes with $\text{NH}_3(\text{aq})$)

While

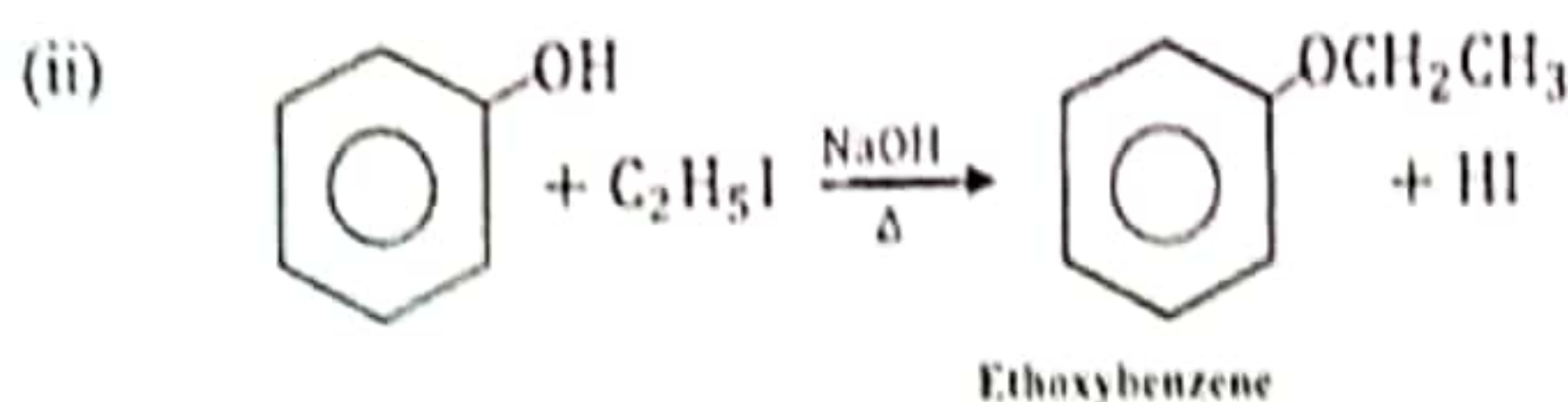
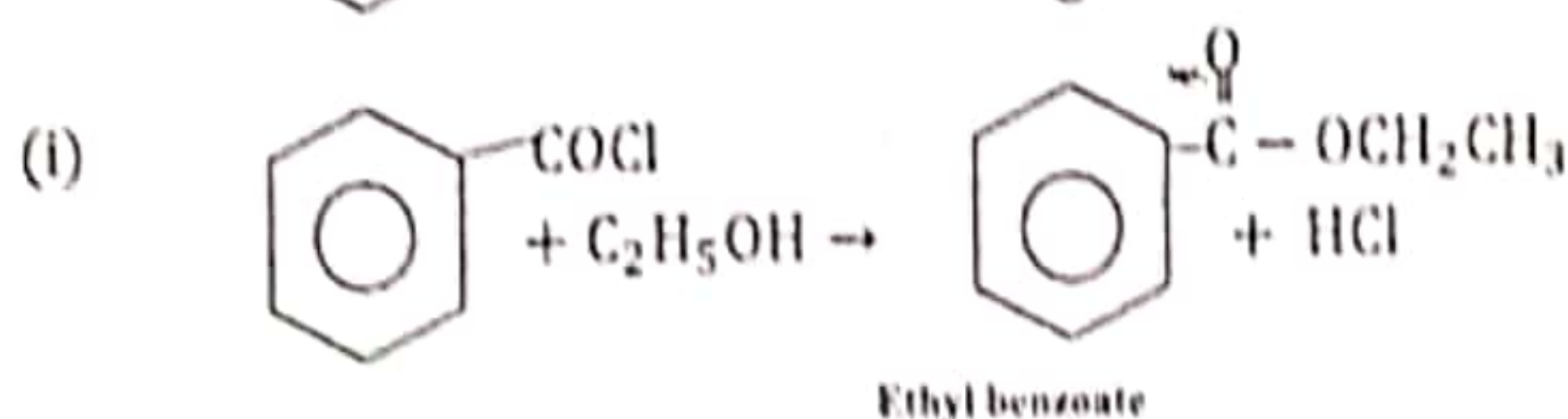
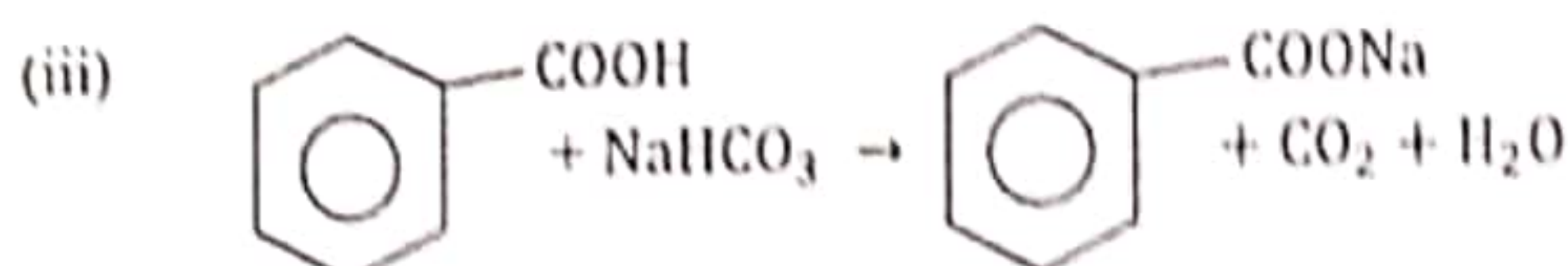
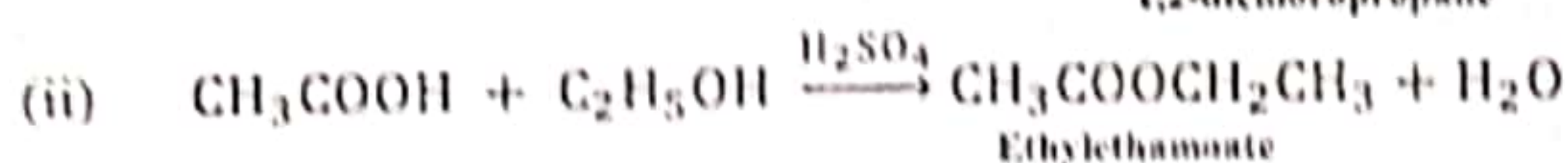
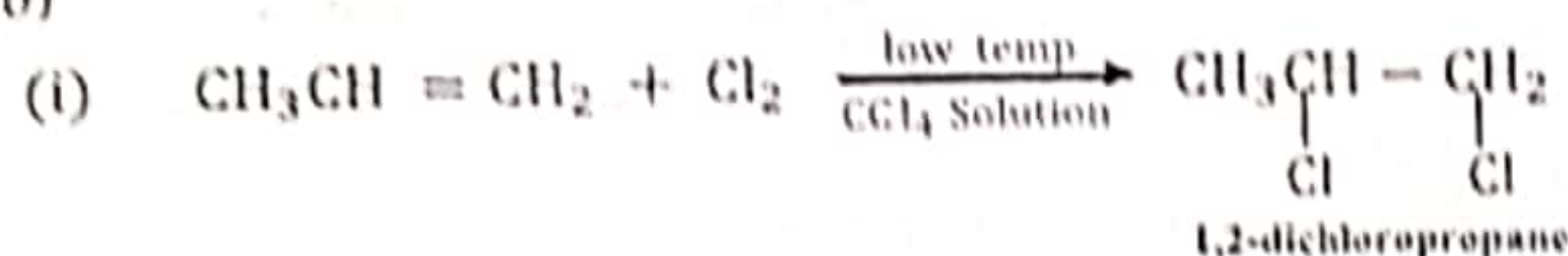


(Here HCl is not formed since there is no OH-group in the given compound)

Note:



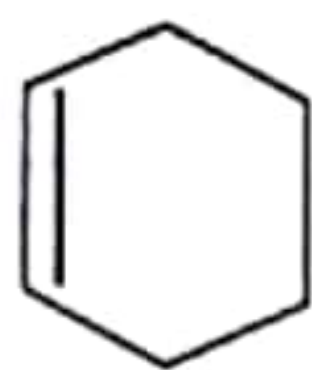
(b)



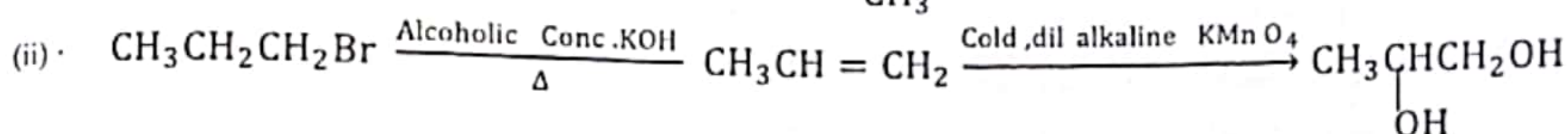
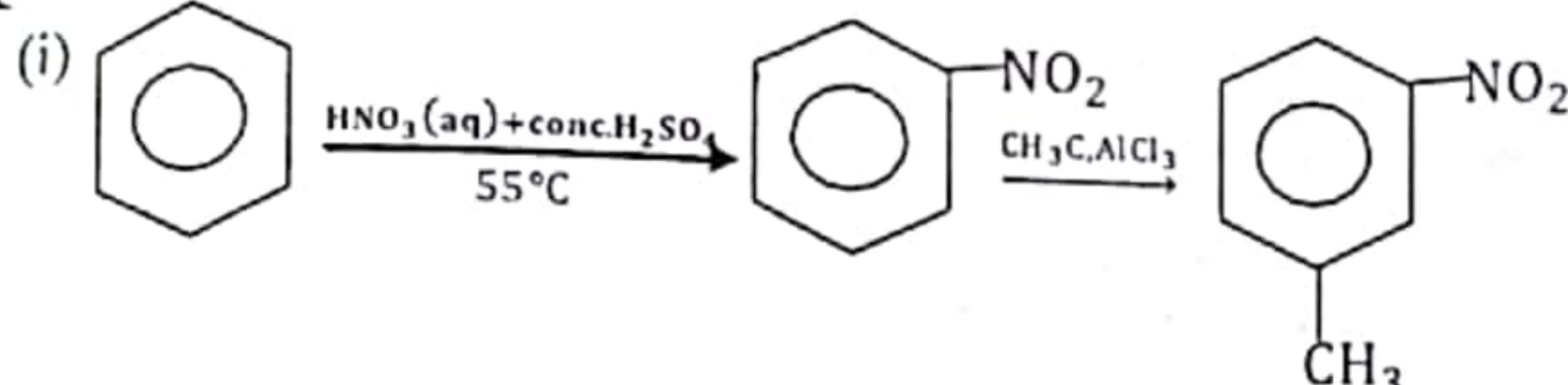
- (c) The molecular formula C_6H_{10} confirm, the general molecular formula of $\text{C}_n\text{H}_{2n-2}$

-Thus the hydrocarbon may be aliphatic alkyne with only one carbon-carbon triple bond, aliphatic diene or cycloalkene with only one carbon-carbon double bond.

- Since only one mole of H_2 were added then the hydrocarbon can never be aliphatic alkyne or aliphatic diene which need 2 moles of H_2 , thus the hydrocarbon must be cycloalkene with only one $C = C$
- The product obtained after ozonolysis confirm the structure of hydrocarbon which is



Question 86



b)

(i)

Elements present in the compound	C	H	O
% Composition of each	64.86	13.5	21.64
Mass of each in 100g of the compound	64.86g	13.5 g	21.64g
Number of moles of each using $n = M / Mr$	$\frac{64.86g}{12g/mol} = 5.405mol$	$\frac{13.5g}{1g/mol} = 13.5mol$	$\frac{21.64g}{16g/mol} = 1.35mol$
Diving by the smallest to get the simples ratio	$\frac{5.405mol}{1.35mol} = 4$	$\frac{13.5mol}{1.35mol} = 10$	$\frac{1.35mol}{1.35mol} = 1$

So empirical formula for the compound is $C_4H_{10}O$

(ii) Let molecular formula be $(C_4H_{10}O)_n$

Then: $48n + 10n + 16n = 74$ or $n = 1$

Hence molecular formula is $C_4H_{10}O$.

(iii) Possible Isomers of S are

$CH_3CH_2CH_2CH_2OH$ (Butan - 1 - ol)

$CH_3CH_2CH(OH)CH_3$ (Butan - 2 - ol)

$CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CH_2OH$ (2 - methylpropan - 1 - ol)

$CH_3 - \overset{\substack{| \\ OH}}{\underset{\substack{| \\ CH_3}}{C}} - CH_3$ (2-methylpropan -2 -ol)

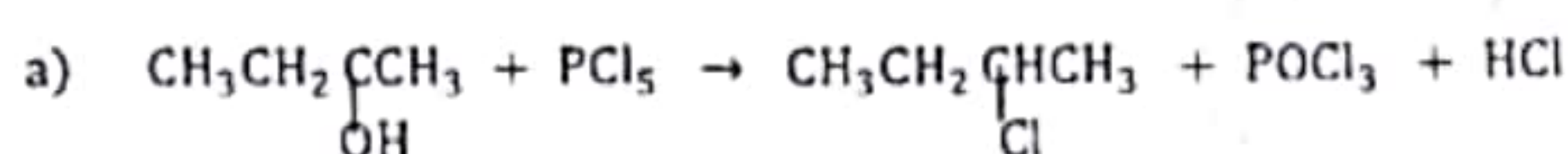
$CH_3CH_2 - O - CH_2CH_3$ (Ethoxyethane)

(iv) S is butan - 2 - ol

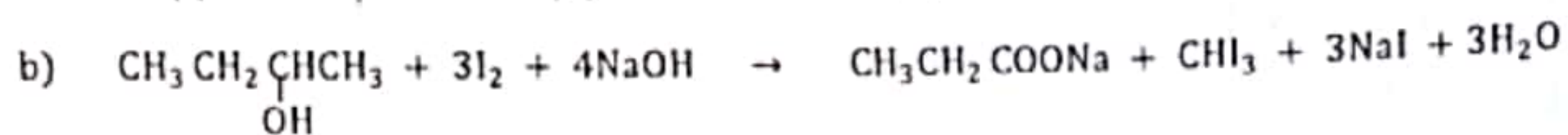
P is chlorobutane

Q is hydrogen chloride gas

R is Sodium propanoate



(S) (P) (Q)

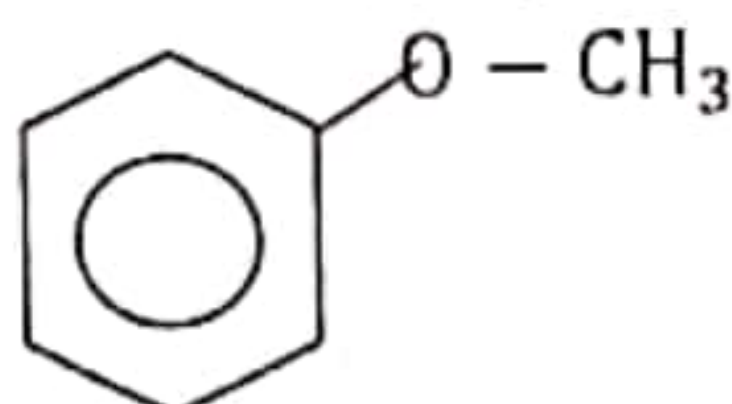


(S) R Yellow ppt

Question 87

a)

i) Structure formula of methyl phenyl ether is



(Methylphenyl ether is common name of methoxybenzene)

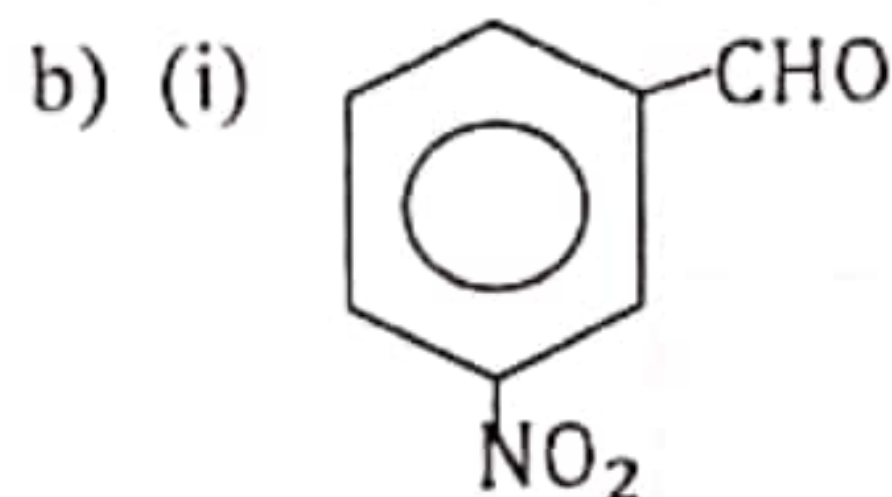
ii) Structure formulae of methanol is CH_3OH

iii) Structure formulae of propanone is $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$

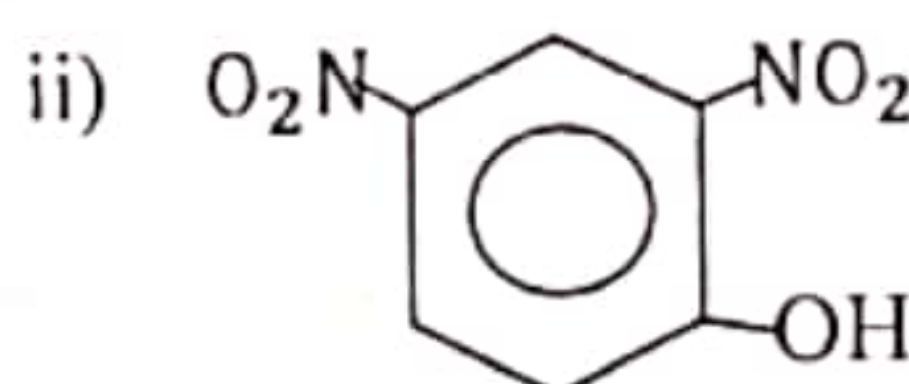
iv) Structure of methyl ethyl ester is $\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$

(Methyl ethyl ester is the common name of methyl ethanoate)

v) Structure formula of 3-phenylpentene is $\text{CH}_3\text{CH}_2\underset{\text{C}_6\text{H}_5}{\text{CH}}\text{CH}=\text{CH}_2$



3-nitrobenzaldehyde



2,4-dinitrophenol

c)

i) $\text{CH}_3\underset{\text{Cl}}{\text{CH}}\text{COOH}$ is stronger acid

Reason

Cl atom which exerts negative inductive effect is closer to carboxylic group ($-\text{COOH}$ group) in $\text{CH}_3\text{CHClCOOH}$ than in CH_2ClCOOH

ii) 2-bromophenol is stronger acid

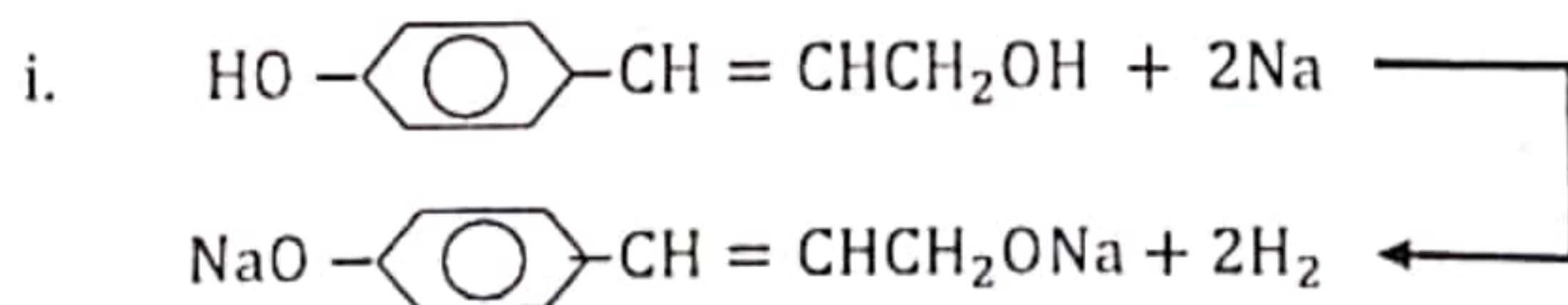
Reason

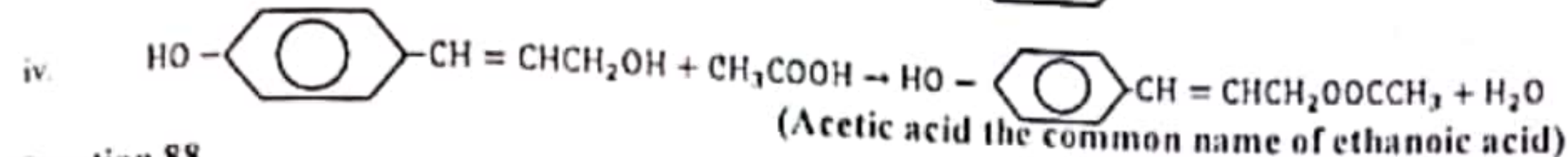
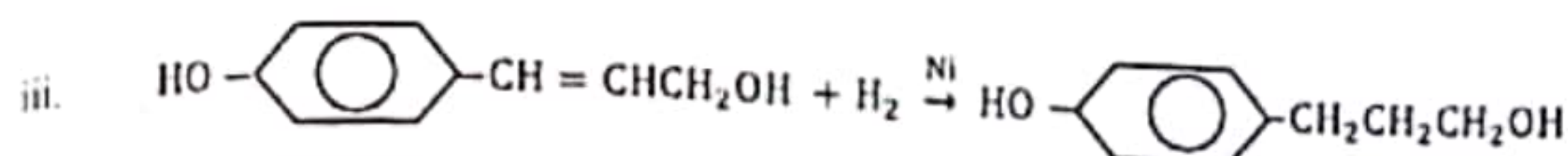
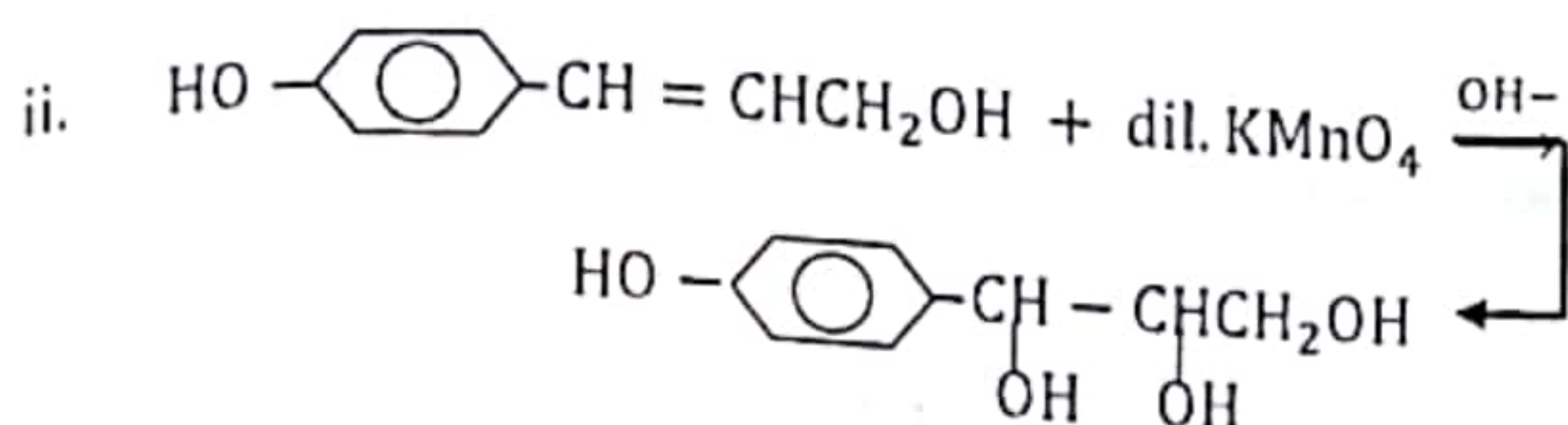
There is electron-withdrawing effect in bromophenol due to presence of strong electronegative bromine atom in it. The situation is different to phenol where there is no bromine atom.

iii) CH_2FCOOH is stronger acid

Reason

F being more electronegative than Cl, it exerts stronger negative inductive effect in CH_2FCOOH than Cl does in CH_2ClCOOH .

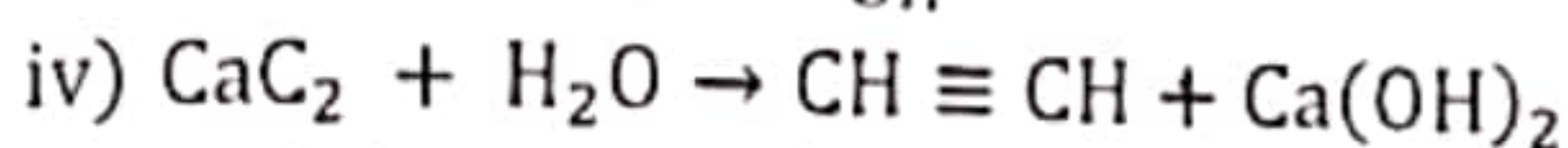
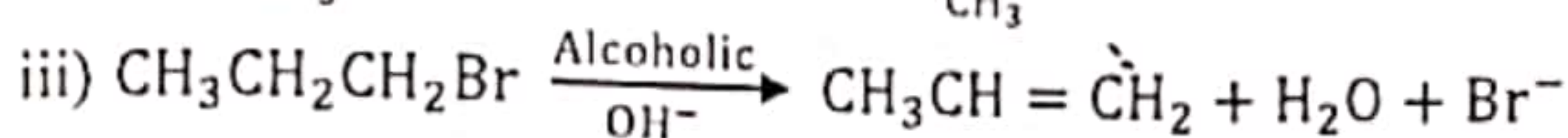
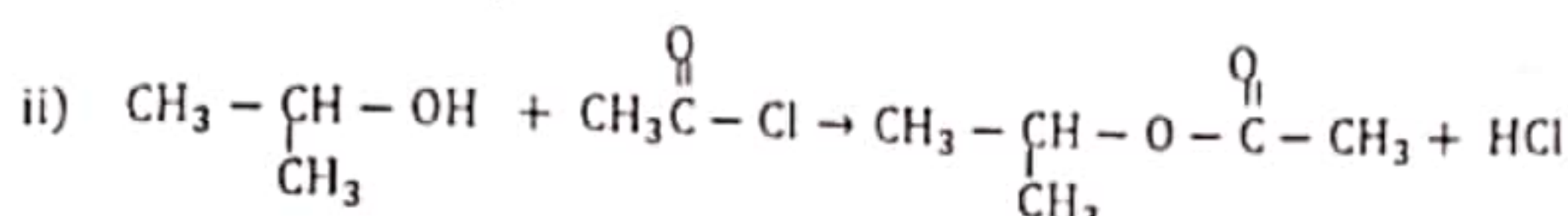
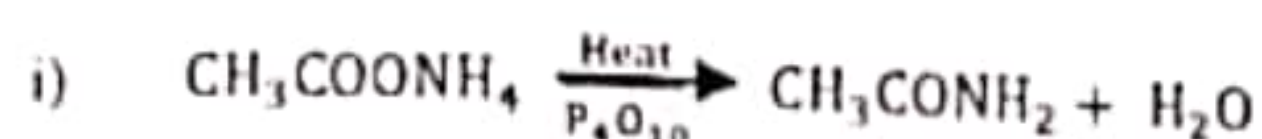




Question 88

a) Refer to the text on directing effect of activators and deactivators.
 (Directing effect of monosubstituted benzene)

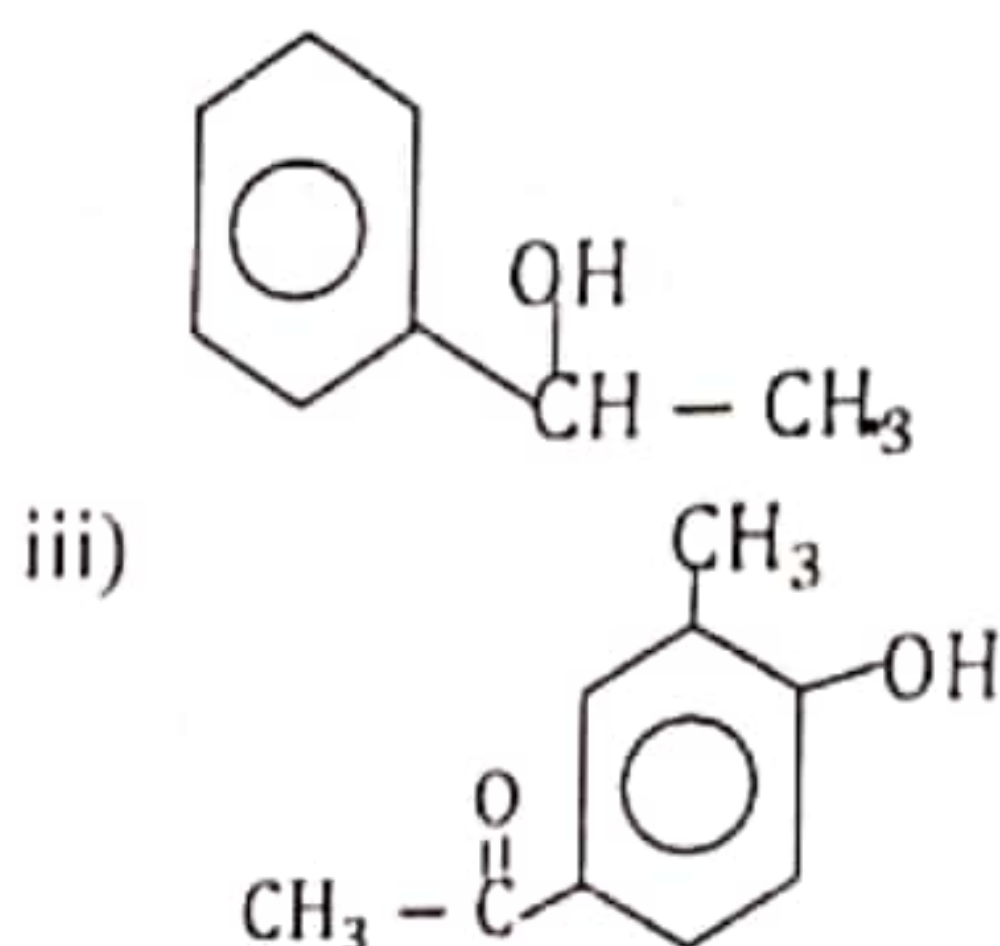
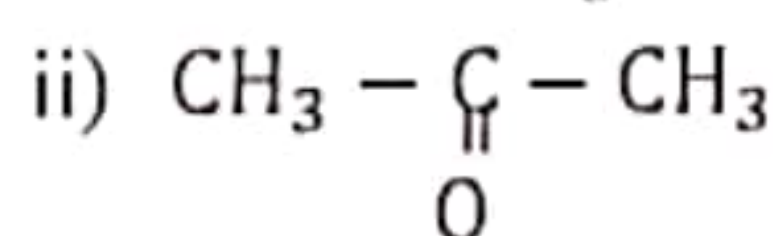
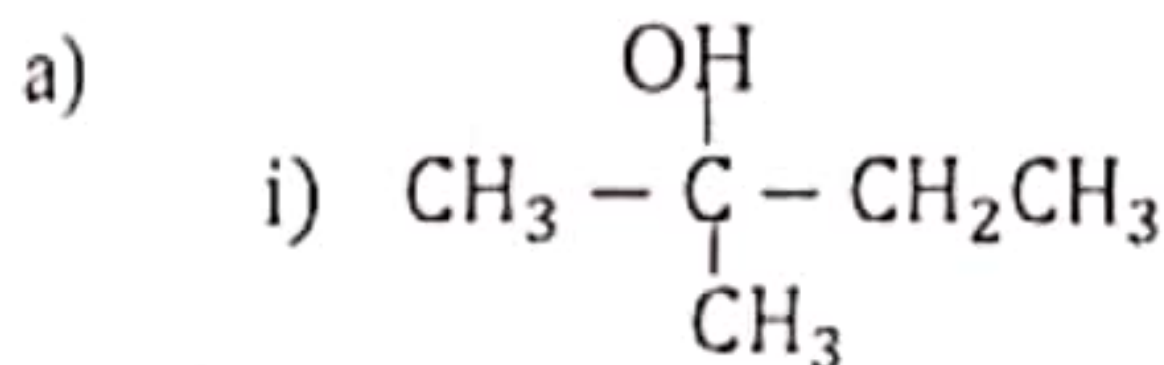
b)



c) Refer to the text on type of organic reactions.

- Ether
- Amine
- Aldehyde
- Ketone
- Carboxylic acid
- Alcohol
- Amino acid (or simply carboxylic acid as carboxylic group dominate amino group)
 (Mixture of amino and carboxylic acid functional group)

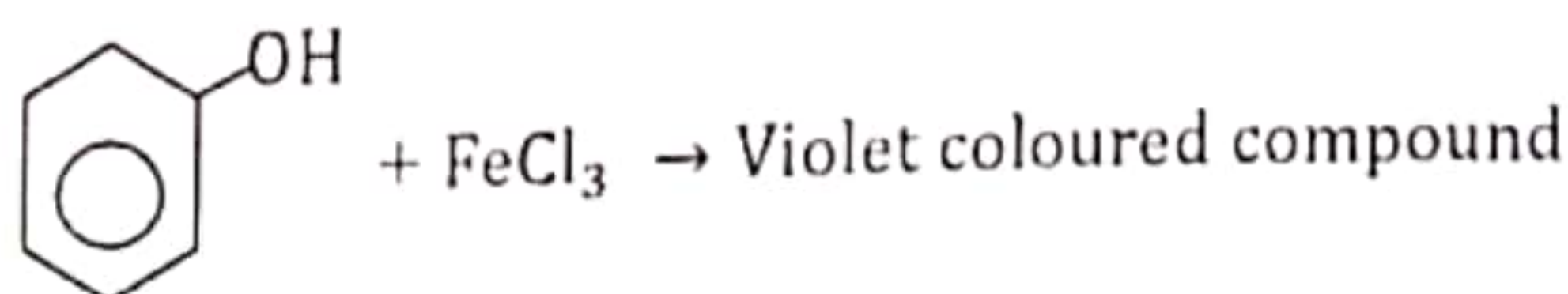
Question 89



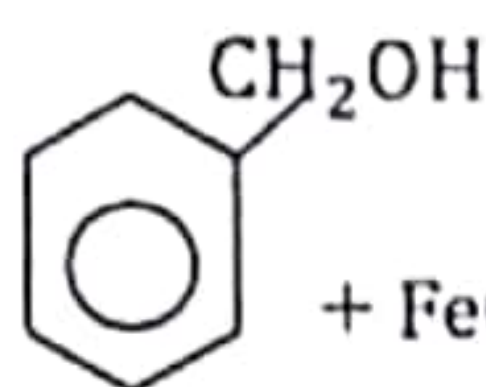
b)

i) The Phenol A gives violet-purple coloured compound with iron (III) chloride while the alcohol B doesn't.

i.e



While

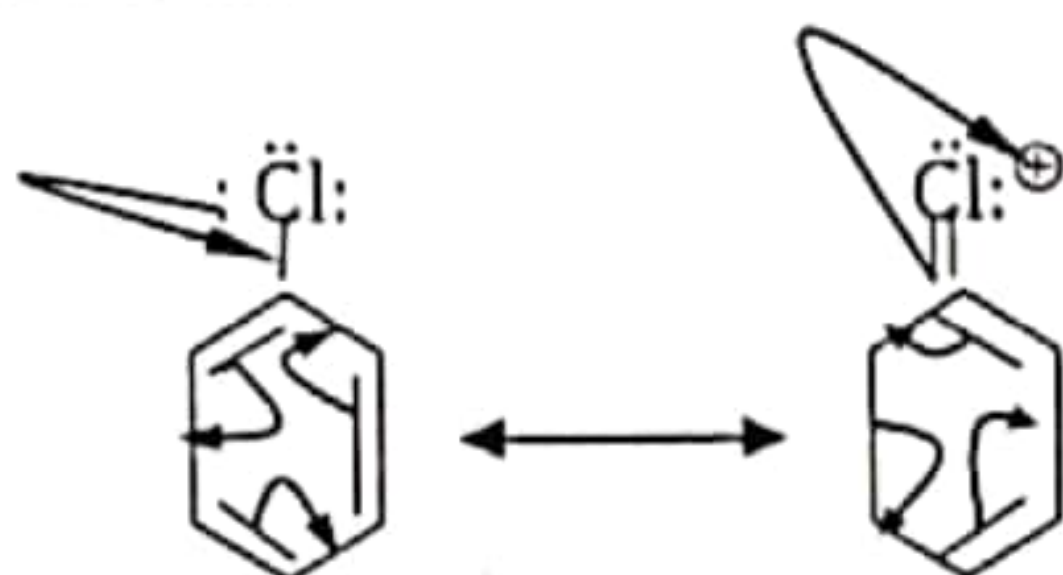


+ FeCl₃ → No Violet – purple coloured compound

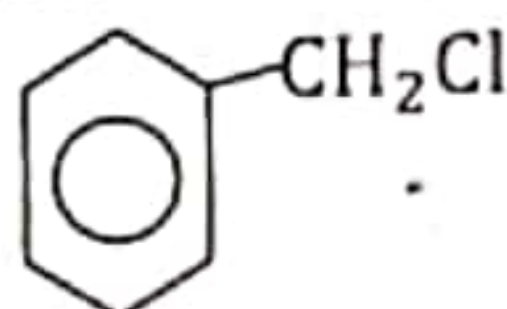
The reader should understand that in A hydroxyl group is directly attached to benzene ring i.e it is phenol while in B hydroxyl group is not directly attached to benzene ring i.e it is alcohol.

c)

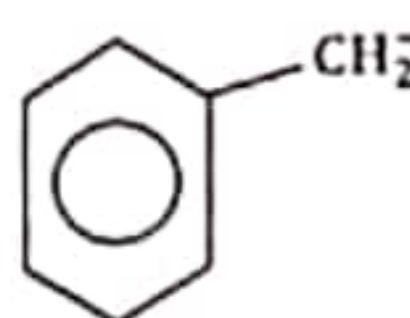
- i) In chlorobenzene, chlorine atom is directly attached to benzene ring thus making difficulty to be replaced from benzene to form AgCl because it is stabilised by mesomerism (+M) which make to have partially C = Cl while in benzyl chloride, the chlorine atom is not stabilised by mesomerism because it is not directly attached to benzene thus making easier to remove it from benzene ring so as to combine with Ag⁺ (from AgNO₃) to form AgCl.
i.e In chlorobenzene



It is more difficult to break C = Cl in chlorobenzene than C – Cl in benzyl chloride whose structure is

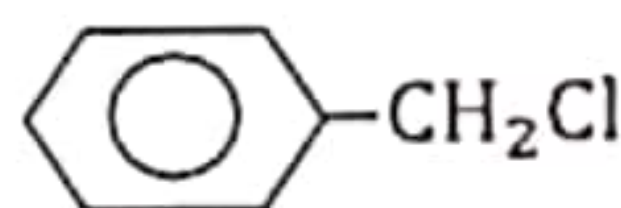


The reader should remember that

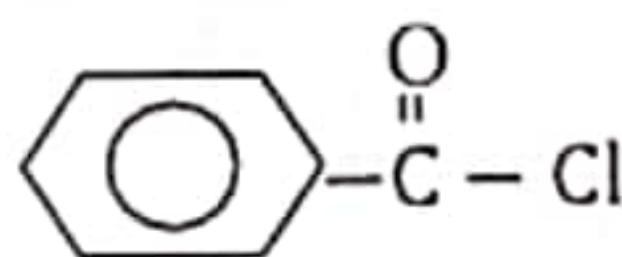


is known as benzyl group.

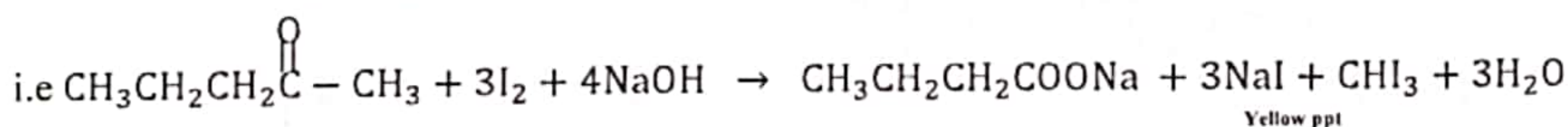
Thus



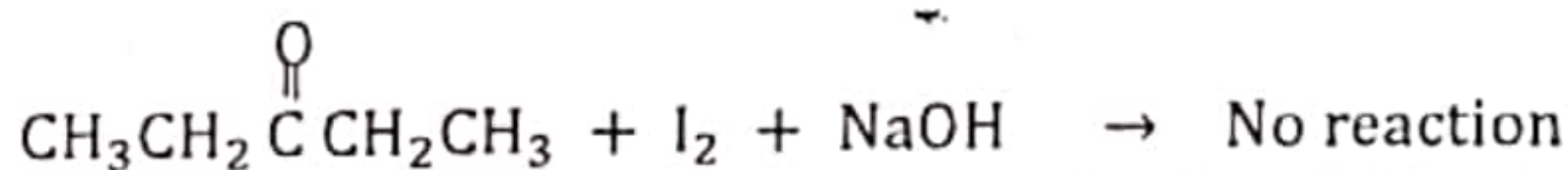
Has common name of benzyl chloride and should not be confused with benzoyl chloride which is IUPAC name with the structure



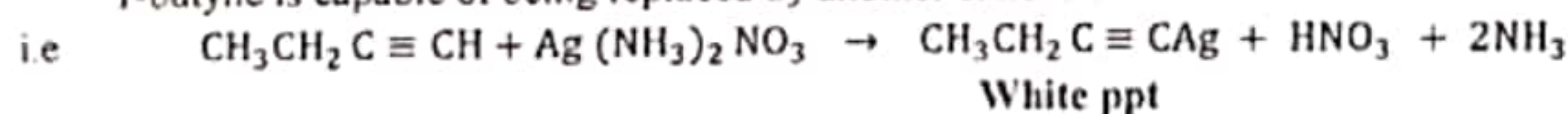
- ii) Fluorine atoms being stronger electronegative, tend to exert stronger negative inductive effect than chlorine atoms thus making 2, 2-difluoroethanoic acid more acidic than 2, 2-dichloroethanoic acid.
iii) Pentan-2-one has terminal methyl group directly bonded to carbonyl group but not pentan-3-one. So the pentan-2-one gives positive results to iodoform test whereas pentan-3-one does not. i.e i.e



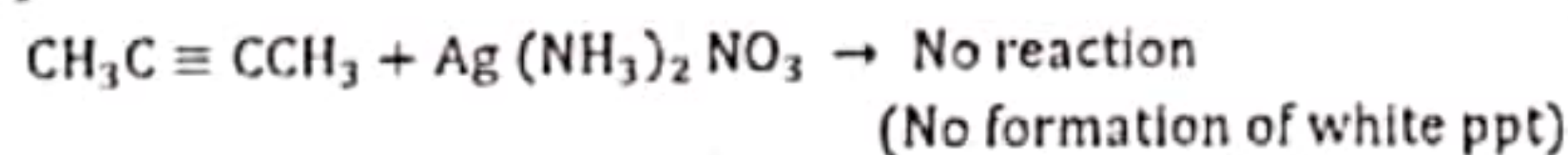
But



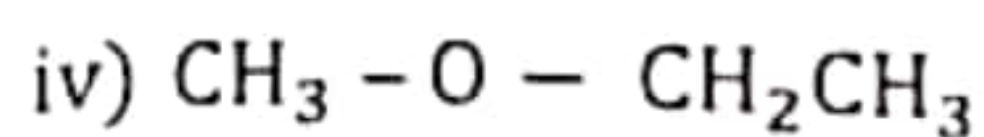
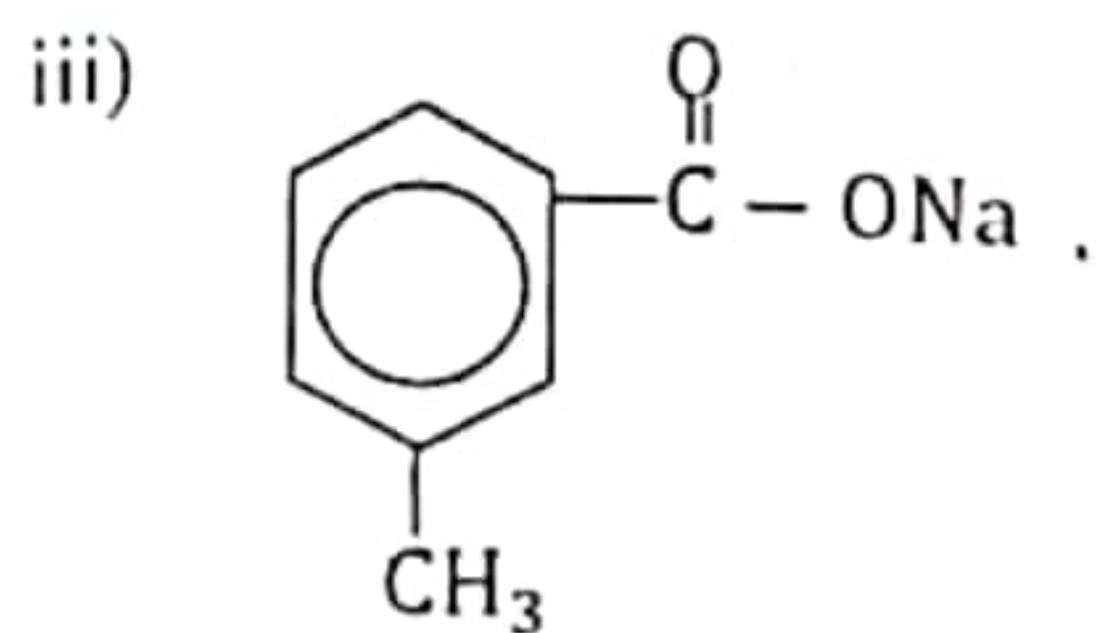
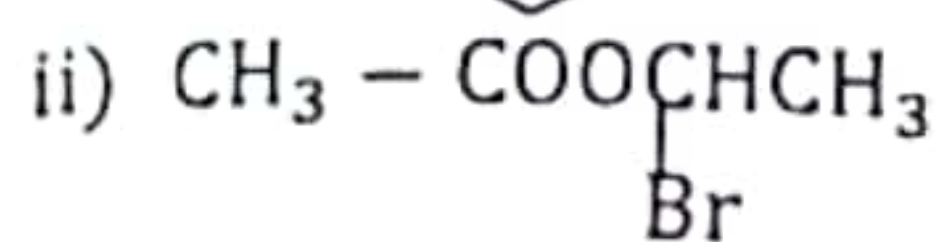
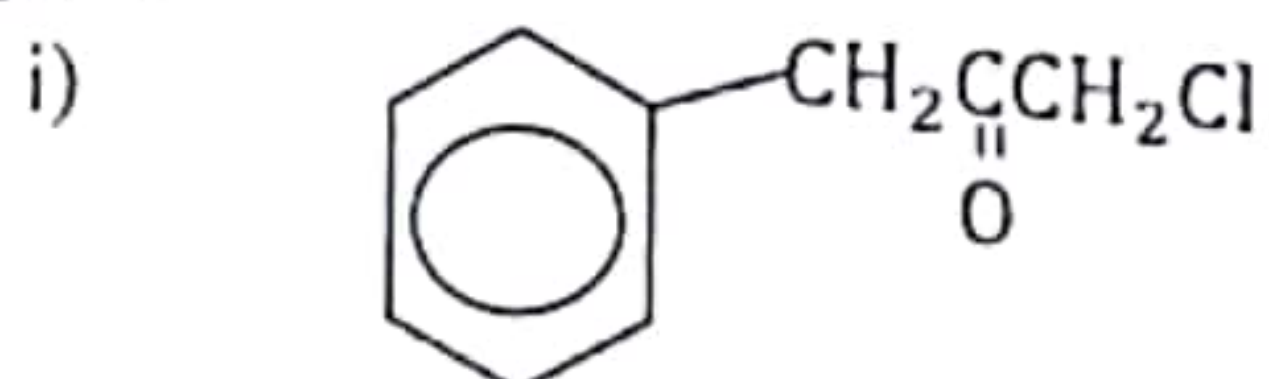
- iv) 1-butyne has free acidic terminal hydrogen (due to presence of terminal (C ≡ C) but 2-butyne does not. The acidic hydrogen present in 1-butyne is capable of being replaced by another cation.



BUT



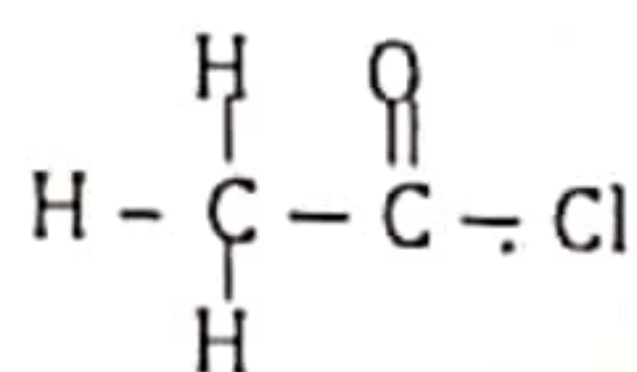
Question 90



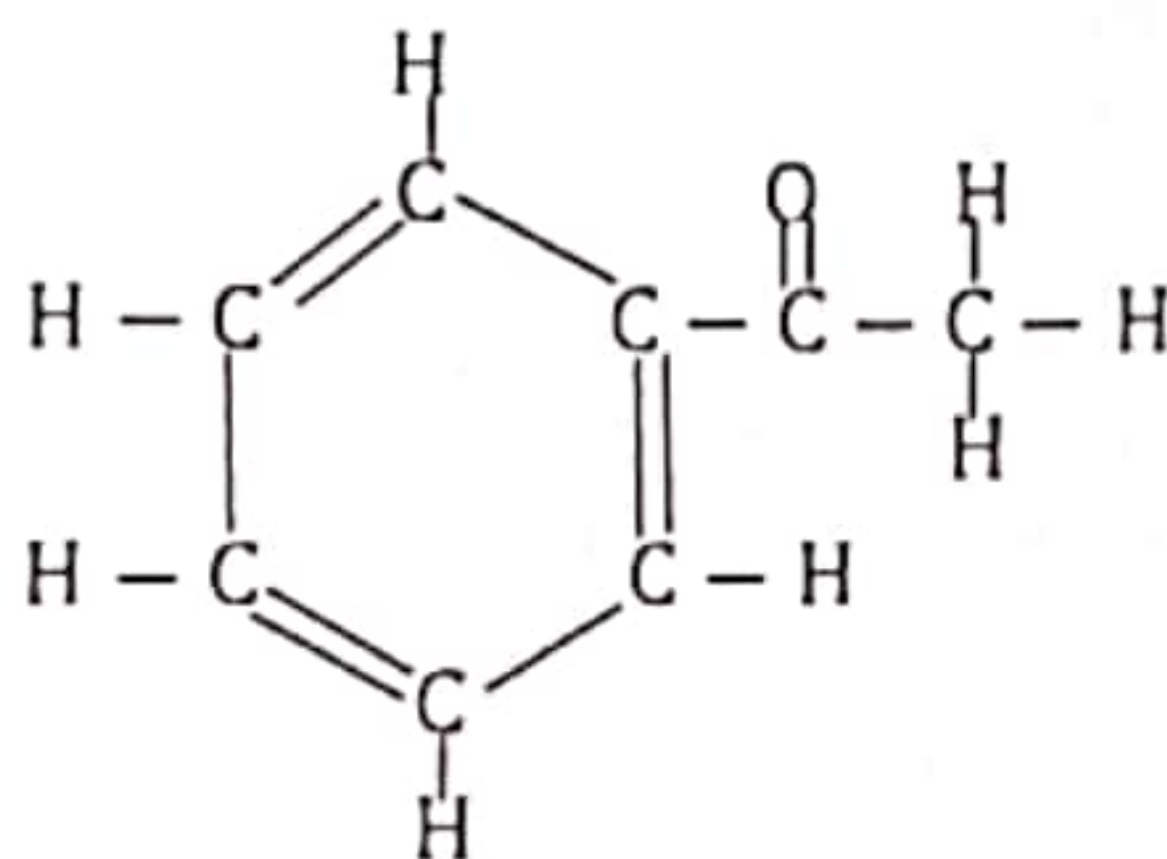
Question 91

a.

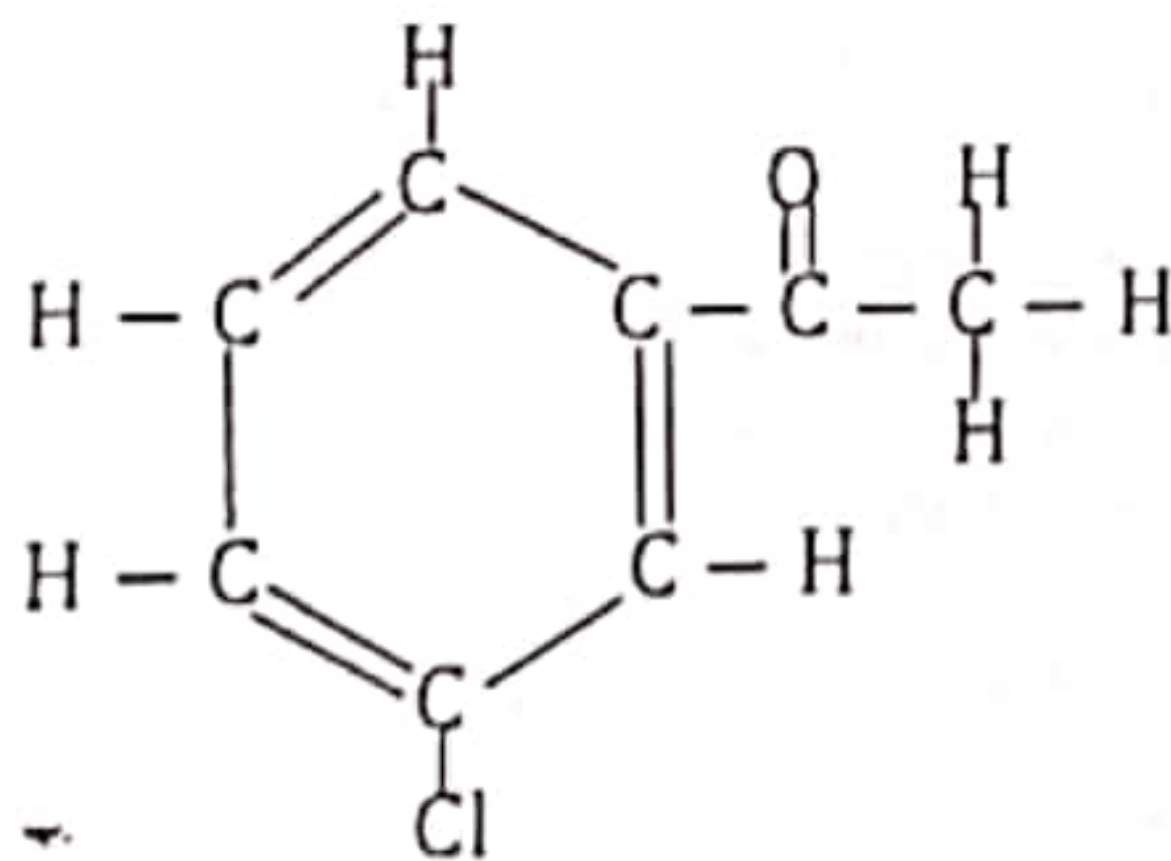
Open structure of B is



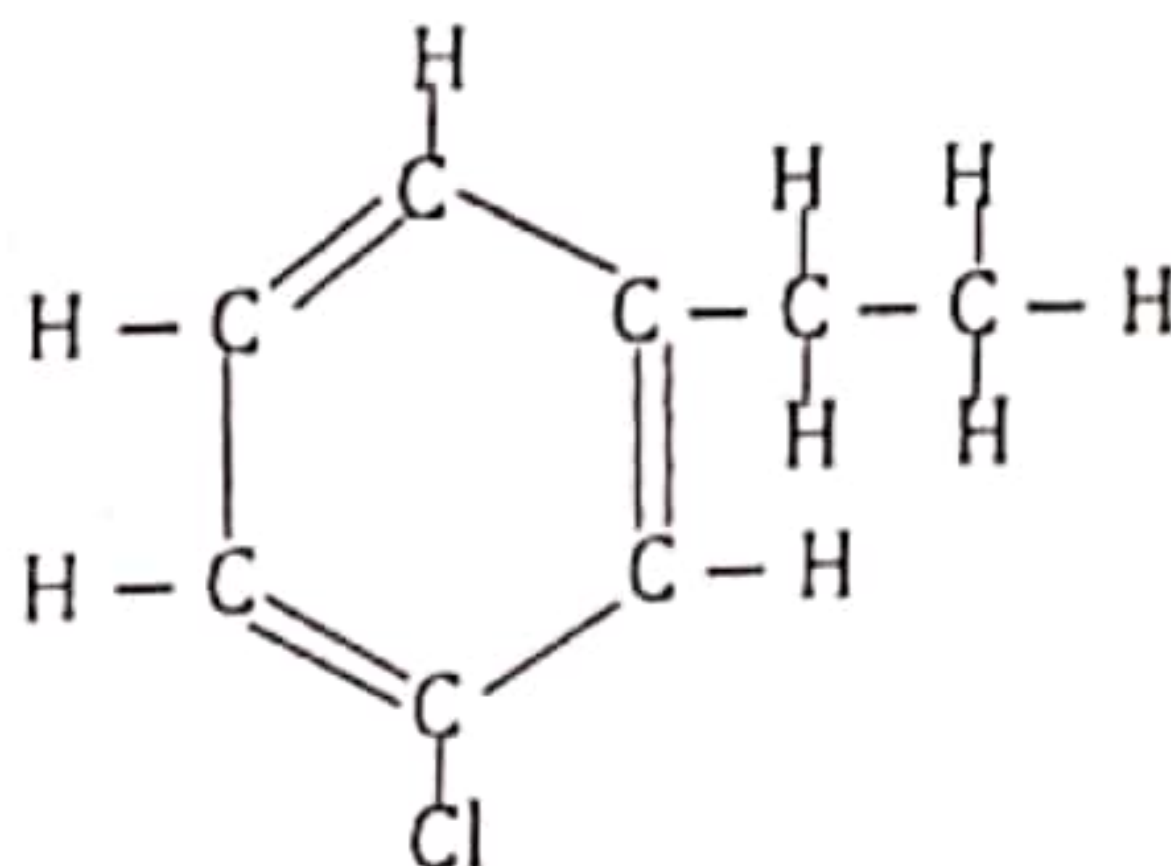
Open structure of C is



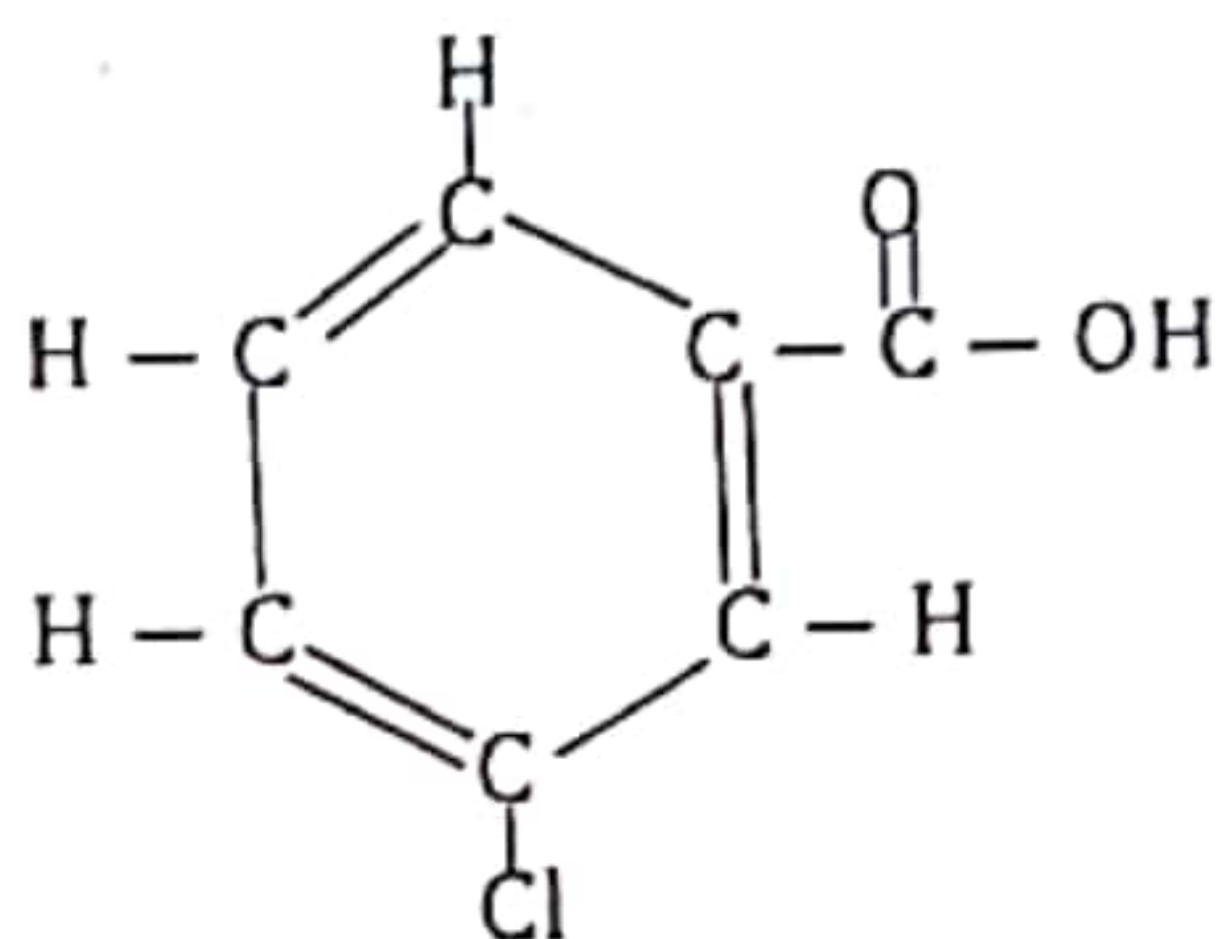
Open structure of D is



Open structure of E is



Open structure of F is



Since R is hydrocarbon then it consists of carbon and hydrogen only. Thus $\% \text{H} + \% \text{C} = 100\%$ from which $\% \text{H} = (100 - 85.7)\% = 14.4\%$

Then

Element present in the compounds	C	H
% Composition of each	85.7	14.3
Mass of each element in 100g of the compound	85.7	14.3g
Number of moles of each	$\frac{85.7\text{g}}{12 \text{ g/mol}} = 7.14 \text{ mol}$	$\frac{14.3}{1 \text{ g/mol}} = 14.3 \text{ mol}$
Dividing by smaller number to get smallest ratio	$\frac{7.14 \text{ mol}}{7.14 \text{ mol}} = 1$	$\frac{14.3 \text{ mol}}{7.14 \text{ mol}} = 2$

- Thus the empirical formula for the hydrocarbon R is CH_2

Let its molecular formulae be $(\text{CH}_2)_n$

Then:

$$12n + 2n = M_r$$

$$\text{But Molecular mass, } M_r = \text{Vapour density} \times 2$$

Thus:

$$14n = \text{Vapour density} \times 2$$

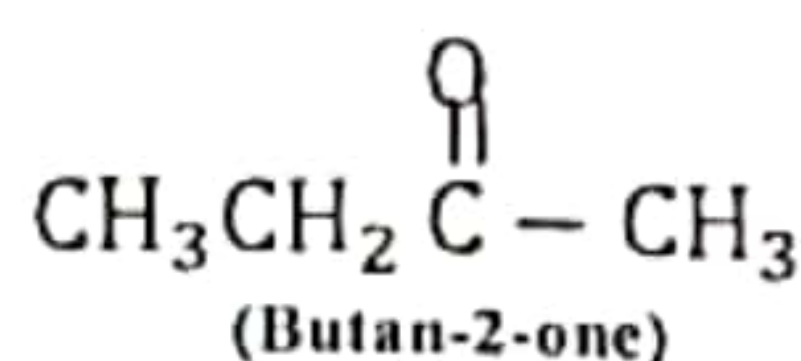
$$14n = 28 \times 2$$

$$\text{So } n = 4$$

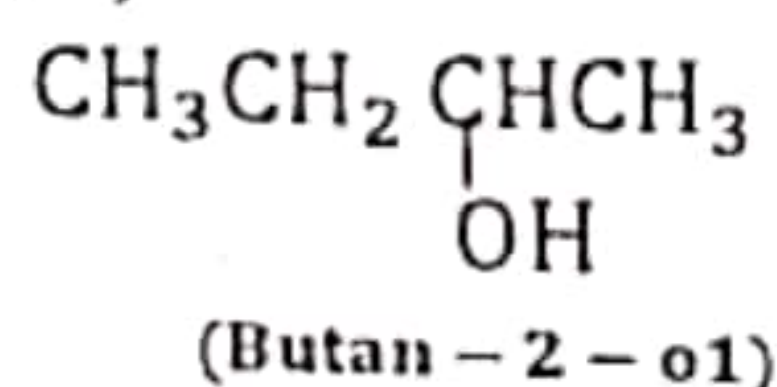
Hence molecular formula for R is C_4H_8

- The molecular formula C_4H_8 confirm the general molecular formula of C_nH_{2n}
- Thus compound R may be cycloalkane or aliphatic alkene with only one $\text{C} = \text{C}$.
- Reaction with HCl indicate that compound R can not be cycloalkane (cycloalkane does not react with HCl), it must be aliphatic alkene with only one double bond.
- After reaction with HCl chloroalkane S is formed (chloroalkane is yielded as additional product).
- When the addition product S is allowed to under go nucleophilic substitution reaction after introducing NaOH, alcohol (T) is formed.
- The alcohol formed (compound T) will undergo oxidation reaction easily if the alcohol is primary or secondary.
- So since the alcohol undergo oxidation easily with acidified KMnO_4 ; it must be primary or secondary alcohol (it can not be tertiary alcohol).
- Thus U may be carboxylic acid or aldehyde (in case of oxidation of primary alcohol) or ketone (in case of oxidation of secondary alcohol)
- Since U react with Brady's reagent it must be carbonyl compound i.e aldehyde or ketone.
- Since U give positive iodoform test it must has terminal methyl group directly bonded to carbonyl group.
- Inability of U to reduce Tollen's or Fehlings solution confirm that U must be ketone (it can't be aldehyde which reduce Tollen's and Fehlings solutions)

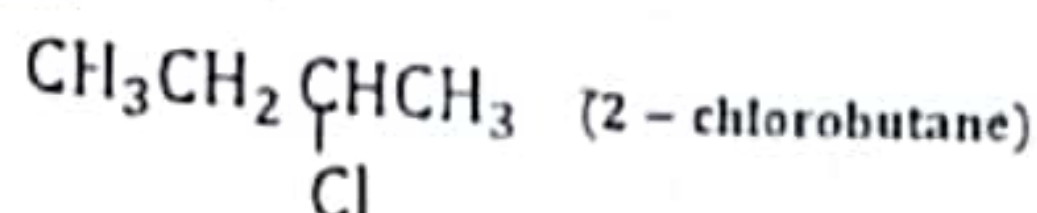
Thus U is Ketone with structure



T is Secondary alcohol with structure



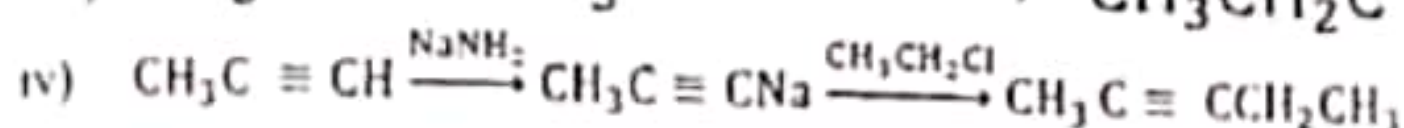
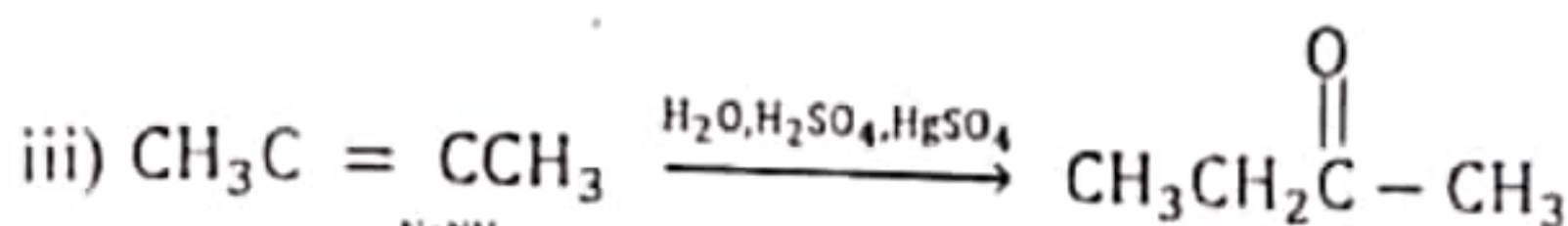
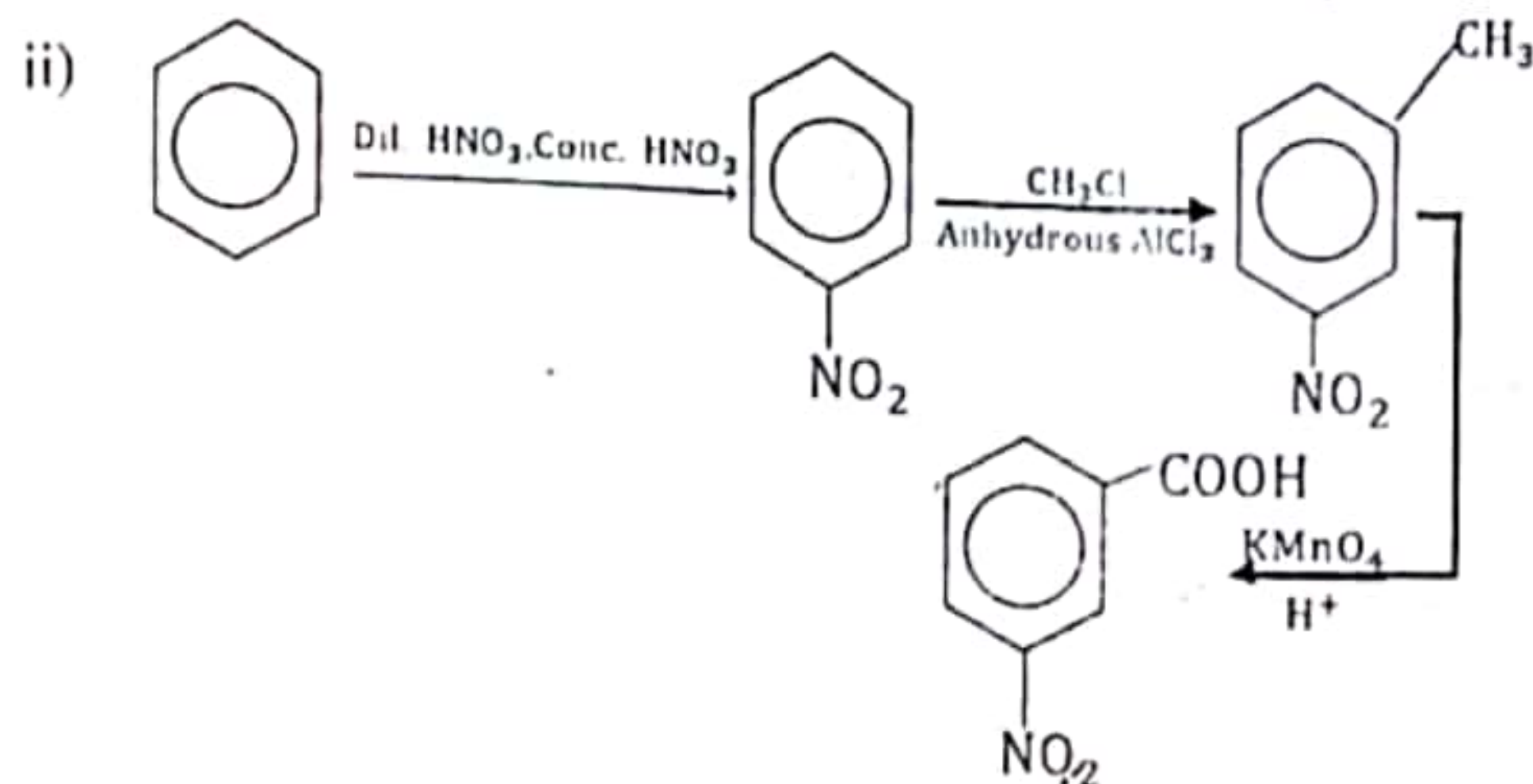
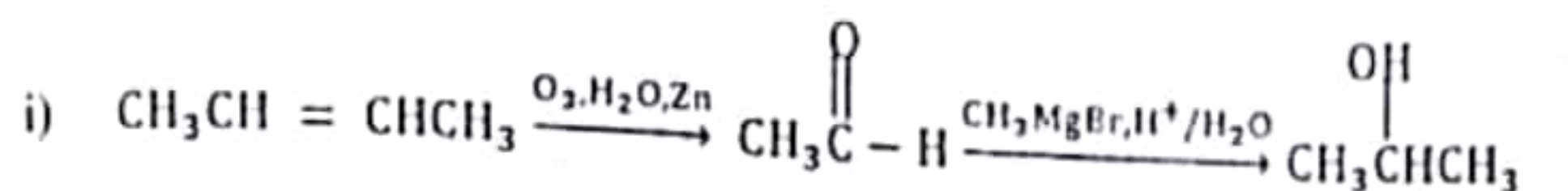
S is secondary haloalkane with structure



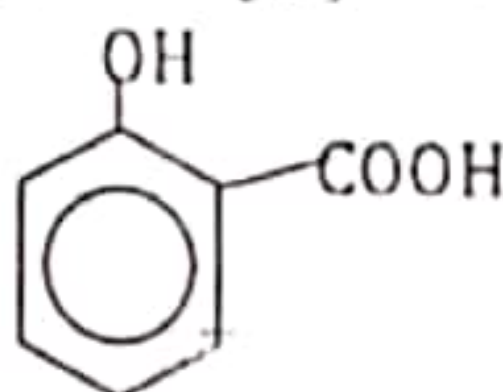
R is aliphatic alkene with structure $\text{CH}_3\text{CH}=\text{CHCH}_3$

ii. Refer to the text

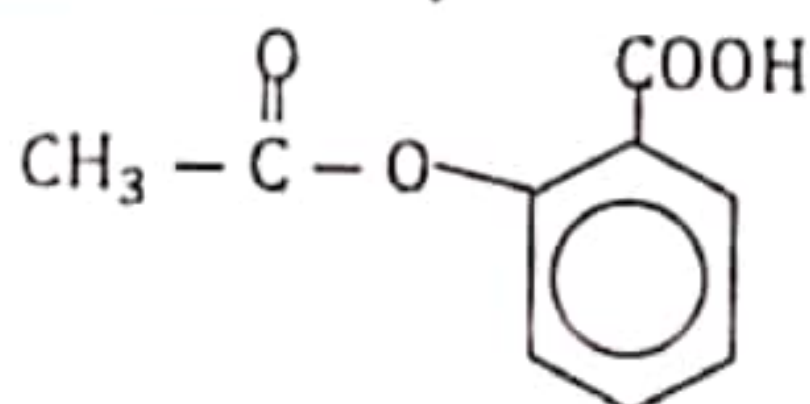
Question 92



v) Structure of salicylic acid is



vi) Structure of aspirin is



Question 93

i) B is more acidic than C

Reason

- B has OH group directly bonded to carbon atom which has double bond and hence delocalization and mesomerism of bond electron pair occur leading to
- Easier of releasing hydrogen proton (H^+) because delocalisation and mesomerism of bond electron pair weakens O-H bond by reducing electron density in the bond.
- Stabilisation of phenoxide ion left after releasing H^+ (due to delocalization of negative charge in mesomerism) thus phenoxide ion can stand on its own without combining with hydrogen proton (H^+) again
- Above factors make concentration of hydrogen proton (H^+) to be high and hence B is more acidic.

ii) D is more acidic than C

Reason

- D has deactivator (NO_2) which withdraw electrons from the OH group attached on the benzene ring. This decrease electron density in O-H bond hence H^+ are liberated easily so D is more acidic.
- On another hand C has methyl group (CH_3) which is activator i.e. it tends to increase electron density in O-H bond thus making difficulty to break the bond so as to release hydrogen protons (H^+) and therefore C is less acidic.

iii) E is more acidic than F

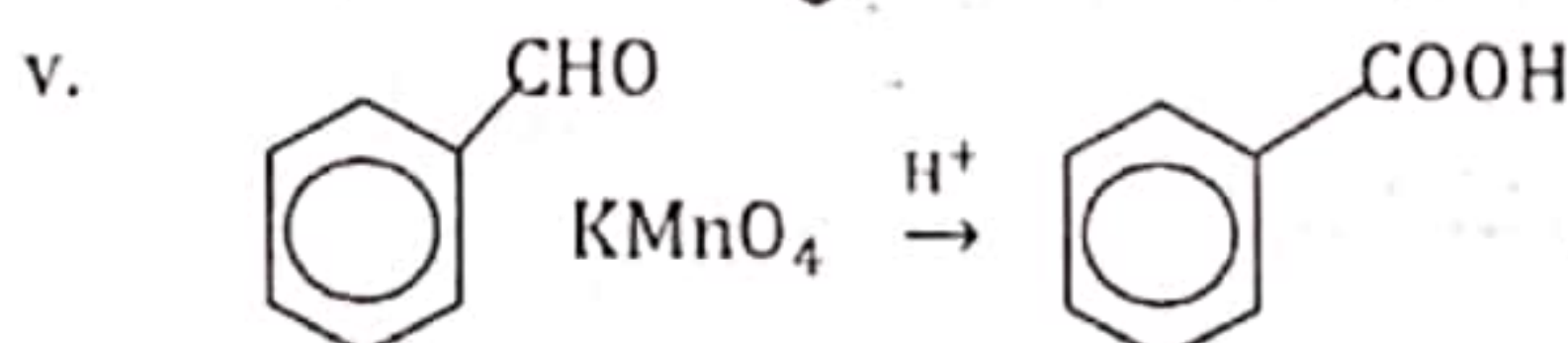
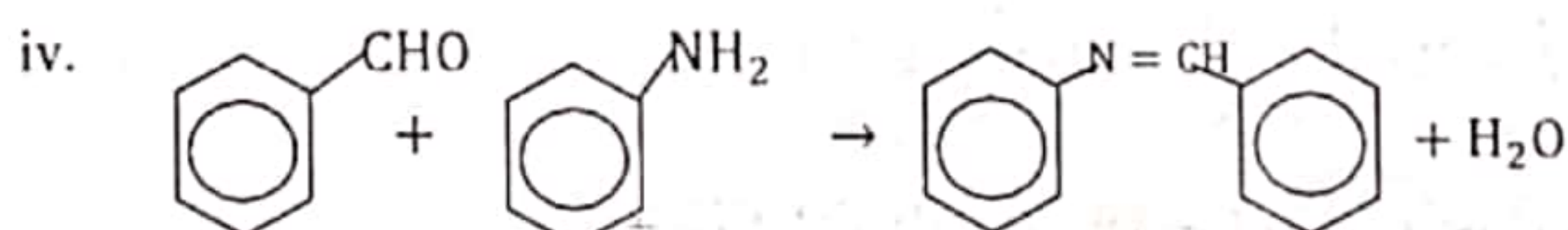
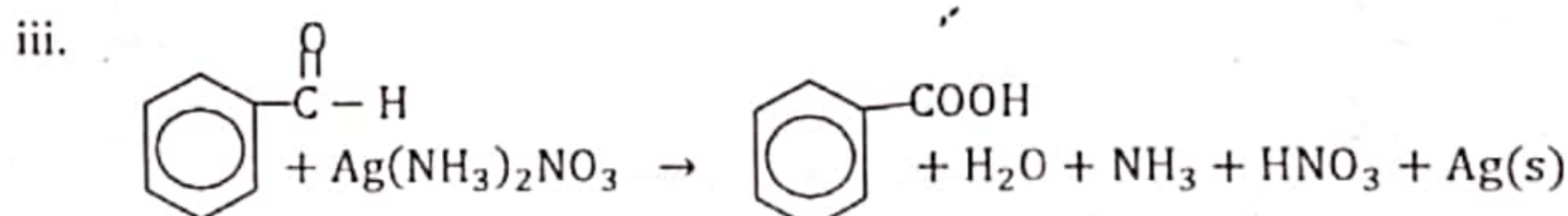
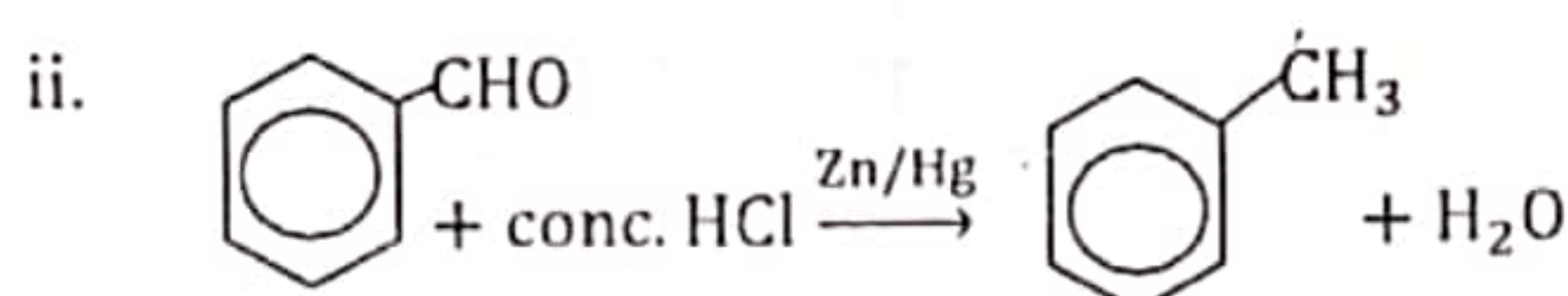
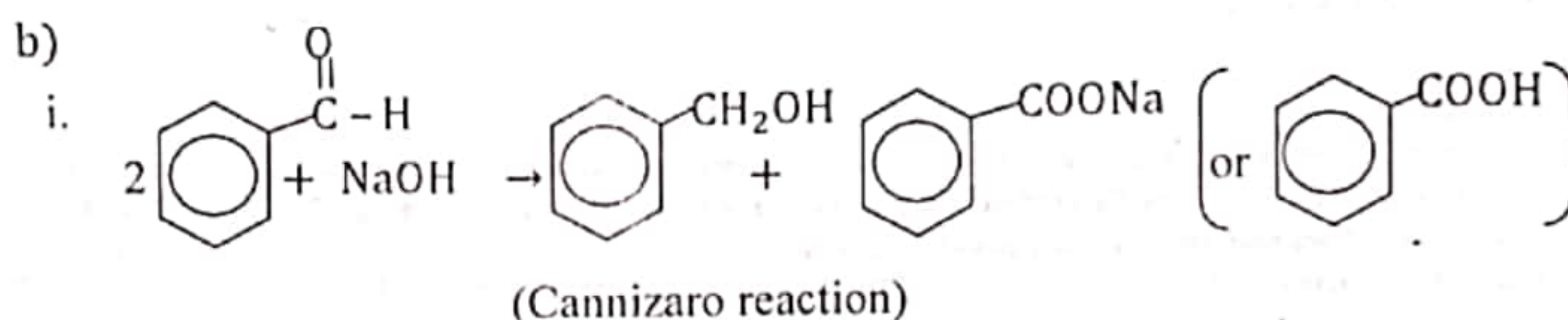
Reason

- E has deactivating group (NO_2) which tend to decrease electron density in carboxylic group including electron density in OH-bond thus making easier to release hydrogen proton (H^+), thus increasing acidic strength of E.

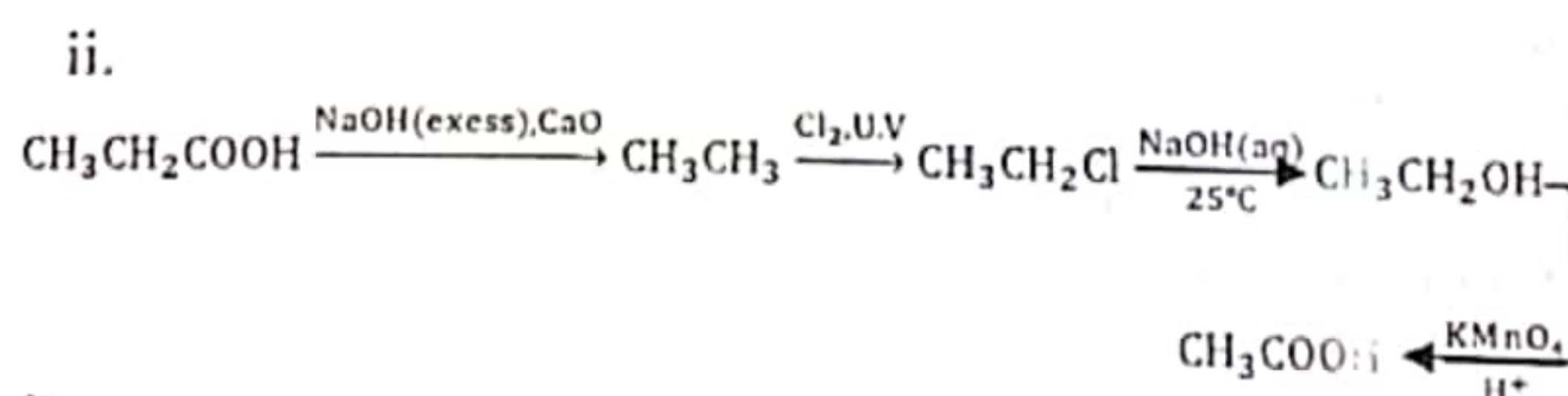
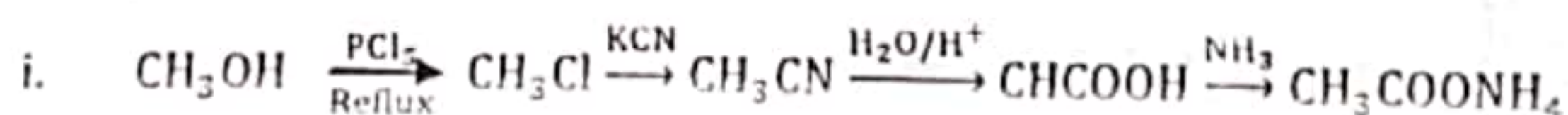
- F contains activating group (NH_2) which supply electron to carboxylic group ($-\text{COOH}$) so increase electron density in $\text{O}-\text{H}$ bond. This make more difficulty for the compound to release hydrogen protons (H^+) and hence acidic strength is decreased
- The reader should remember that if the compound has larger value of K_a (Dissociation constant for acid) then the compound will be more acidic and since $\text{p}K_a$ is taken as negative logarithm of K_a i.e $\text{p}K_a = -\log K_a$
- It follows that if K_a is large then $\text{p}K_a$ will be small and vice versa, so if the compound has smaller value of $\text{p}K_a$ the compound will be more acidic.

Generally the compound will be more acidic (i.e its acidic strength will be high) if has

- Small value of $\text{p}K_a$
- Large value of K_a

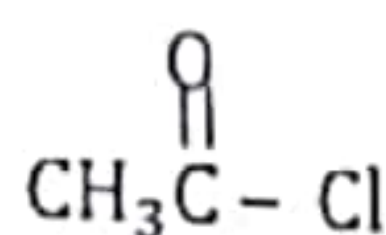


Question 94

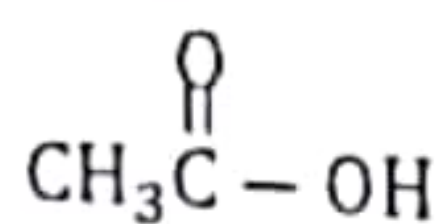


i)

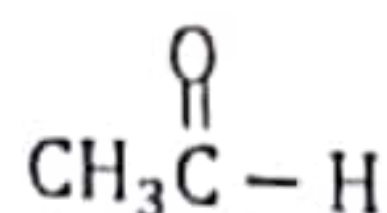
- Structure of R is



- Structure of D is



- Structure of B is



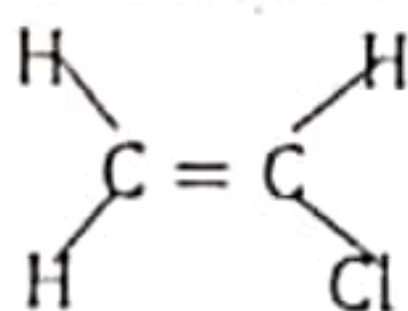
- Structure of Q is $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{C}-\text{H}$
- Structure of A is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$

ii) IUPAC name of each compound

- A is hex-2-ene
- B is ethanal
- Q is butanal
- D is ethanoic acid
- R is ethanoyl chloride

Question 95

- a) Refer to the text
- b) Thermosetting polymers are polymer materials which are hard and soften when heated with decomposition once hardened they cannot be softened by re-heating, example plastic. On another hand; thermoplastic polymers are polymer materials which soften when heated without decomposition and become hard when cooled example nylon
- c) Examples of natural polymers are:
 - i. Starch
 - ii. Cellulose
 - iii. Protein
 - iv. Rubber
 - v. DNA
- d) Vinyl chloride has the following structure



So the problem has directly solved from the notes on anionic addition polymerisation.

- i) Monomer is $\text{H}_2\text{N}-\overset{\text{C}}{\overset{|}{\text{R}}}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ (Amino acid)
- ii) Monomers are $\text{HO}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ and $\text{OHCH}_2\text{CH}_2\text{OH}$
- iii) Monomers are $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
And $\text{HO}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{C}-\text{OH}$

Question 96

- i) $\text{C}_6\text{H}_5\text{MgBr} + \text{CO}_2 \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{C}_6\text{H}_5\text{COOH}$
(Phenyl magnesium Bromide) (Benzoic acid)
- ii) $\text{C}_6\text{H}_5\text{COOH} + \text{PCl}_5 \rightarrow \text{C}_6\text{H}_5\text{COCl} + \text{POCl}_3 + \text{HCl}$
(Benzoic acid) (Benzoyl chloride)
- iii) $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- iv) $2\text{C}_6\text{H}_5\text{CHO} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{COONa} + \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
(Benzaldehyde) (sodium benzoate) (Phenyl methanol)
- v) $\text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{Boil}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{HCl}$
(Toluene) (Benzylchloride)

Question 97

- a) Number of moles of silver nitrate used is $\frac{31.2 \times 0.1}{1000}$ moles
- Silver nitrate will react with NaBr obtained from the reaction between bromoalkane and sodium hydroxide ($\text{RBr} + \text{NaOH} \rightarrow \text{ROH} + \text{NaBr}$) according the following equation:



Yellow ppt

- From which mole ratio of AgNO_3 to NaBr is 1:1
- Thus number of moles of NaBr produced in the reaction between NaOH and bromoalkane was also $\frac{33.28 \times 0.1}{1000}$ moles

From the equation of the reaction between NaOH and bromoalkene.



Where R is alkyl group

- Mole ratio of bromoalkane (RBr) to NaBr is 1:1
- Thus number of moles of bromoalkane (limited reactant) originally present in 25cm^3 of the solution was also $\frac{33.28 \times 0.1}{1000}$ moles
- So number of moles of bromoalkene present in 250 cm^3 of the solution was $\frac{33.28 \times 0.1 \times 250}{1000 \times 25}$ moles

- The above number of moles was obtained from 4.1g of the bromoalkene So using

$$n = \frac{m}{M_r} \text{ or } M_r = \frac{m}{n}$$

- Molecular mass of bromoalkane will be

$$\frac{4.1 \times 100 \times 25}{33.28 \times 0.1 \times 250} \text{ g/mol} = 123.2 \text{ g/mol}$$

Hence relative molar mass of the bromoalkane is 123.

- c) Alkyl group has general molecular formula of $\text{C}_n\text{H}_{2n+1}$ thus general formula of bromoalkane can be written as $\text{C}_n\text{H}_{2n+1}\text{Br}$.

$$\text{From which } 12n + 2n + 1 + 80 = M_r$$

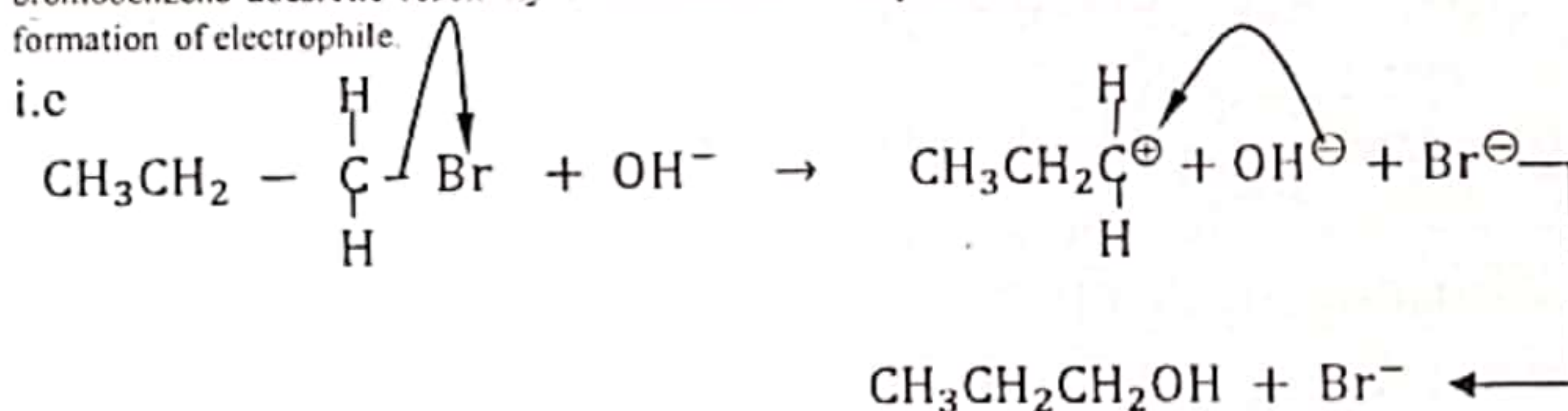
$$14n + 81 = 123 \text{ or } 14n = 42 \text{ or } n = 3$$

Therefore molecular formula for the compound is $\text{C}_3\text{H}_7\text{Br}$

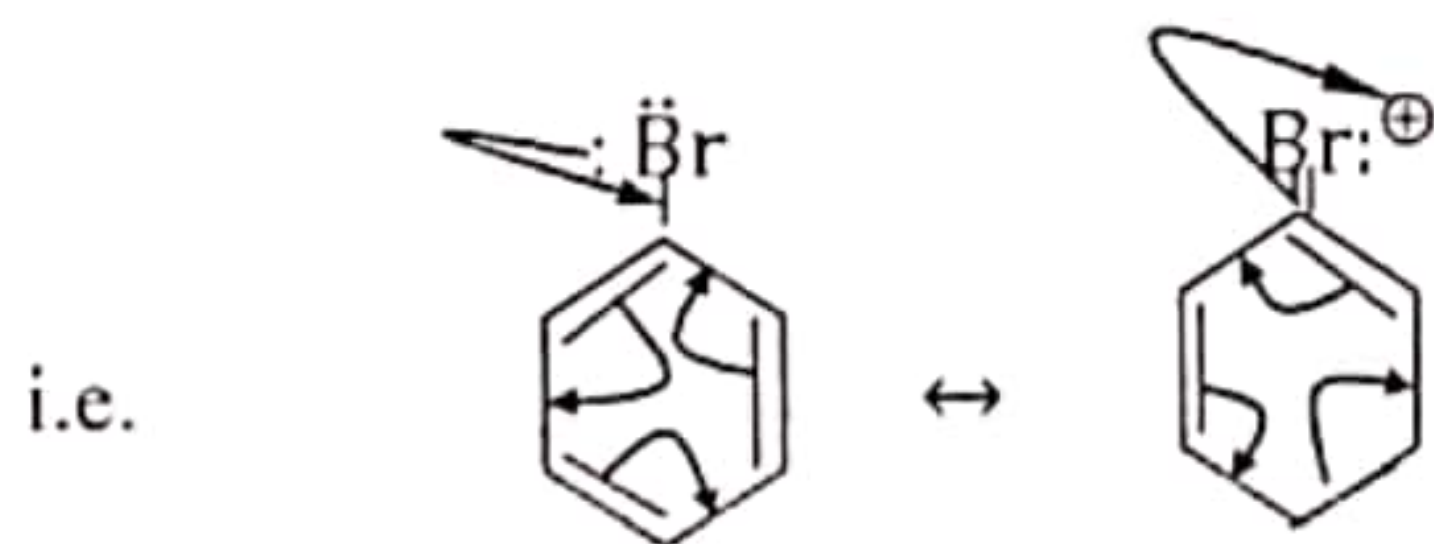
- c) Structural formula for possible isomers for the compound are.



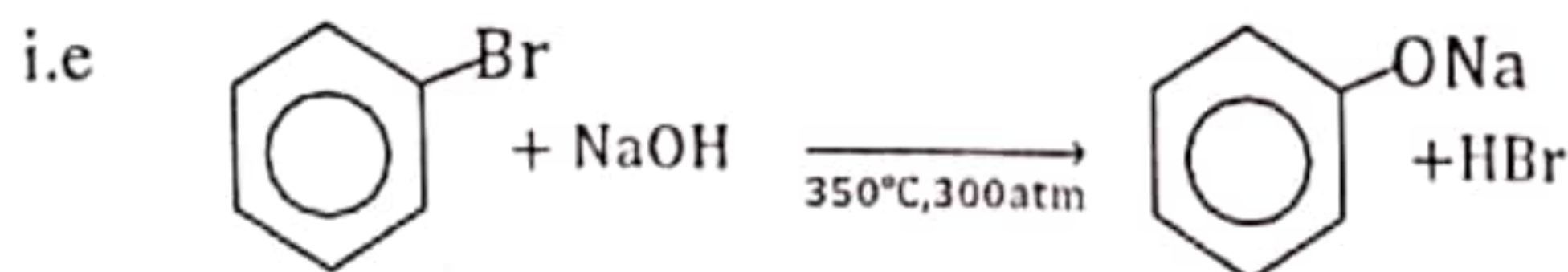
- d) Bromopropane (even 2-bromopropane) can react with sodium hydroxide (nucleophilic substitution reaction) easier i.e. faster than bromobenzene does. The reactivity of bromoalkane is explained by easiest of $\text{C}-\text{Br}$ to undergo heterolytic bond cleavage resulting to formation of electrophile.



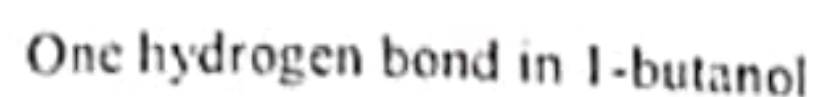
The low reactivity of bromobenzene is explained by presence of delocalised π -electrons in benzene ring which make it to have nucleophilic character (less electrophilic) thus it resists to undergo nucleophilic substitution reaction also presence of mesomerism in benzene ring leads to formation of $\text{C}=\text{Br}^+$ thus making more difficulty for bond between carbon and bromine to undergo heterolytic bond cleavage so as to leave the chance for incoming nucleophile ($-\text{OH}$)



Instead bromobenzene can react with sodium at relative higher temperature and pressure compared to bromopropane and sodium phenoxide is formed (not phenol like bromopropane which forms propanol).



However, two molecules of 1-butanol are held by a single Hydrogen bond whereas two molecules of propanoic acid are held together by two hydrogen bonds in cyclic form as shown below



(From conversion of propene to iodopropane by markownikoff's addition in step 4)